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AFRPL-TR-66-159

THE DEVELOPMENT AND EVALUATION OF A HYDROCARBON BINDER FOR HIGH ENERGY SOLID PROPELLANTS (u)

First Quarterly Report
for Period,
14 March 1966 to 13 June 1966
Contract AF 04(611)-11419

by

D. E. Johnson and A. J. DiMilo
Aerojet-General Corporation
Solid Propellant Operations
Sacramento, California

July 1966

Sponsored by

Air Force Rocket Propulsion Laboratory
Research and Technology Division
Edwards, California
Air Force Systems Command
United States Air Force

W. O. 1030

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FOREWORD

This technical report was prepared under Contract No. AF 04(611)-11419 as partial fulfillment of the requirements of Project 3418 of the Air Force Rocket Propulsion Laboratory, Research and Technology Division, Air Force Systems Command, Edwards, California. This report was designated Aerojet-General Corporation Report 1030-81Q-1 and covers the results of work done during the interval 14 March 1966 to 13 June 1966. The project was a follow-on to the project completed under Contract AF 04(611)-10386, the results of which are reported in Report No. AFRPL-TR-66-40. This project was monitored by Mr. J. L. Trout and Mr. Robert Corley.

Acknowledgement is made to the following persons who have contributed materially to the work performed during this period: A. J. Di Milo, Senior Chemist; D. E. Johnson, Senior Research Chemist; R. H. Quacchia, Research Chemist A; J. L. Humphreys, Associate Chemist; and A. H. Swift, Development Chemist.

This technical report has been reviewed and is approved.

Prepared By:

A. J. Di Milo
Program Manager

D. E. Johnson
Principal Investigator

Approved By:

L. J. Rosen, Manager
Advanced Propellants Department
Research & Technology Operations

AFRPL-TR-66-159

(C) ABSTRACT

(U) The investigation and characterization of the saturated hydrocarbon binder developed under Contract AF 04(611)-10386 for use in solid rocket propellant were continued. The molecular weight and functionality distributions were determined for the saturated hydrocarbon prepolymer. The functionality of the prepolymer was independent of the molecular weight. Recrystallization was better than distillation for purifying the isocyanate crosslinking agent. While NH_4ClO_4 was compatible with the isocyanate curing agents, many plasticizers were not. Of the plasticizers, the hydrocarbon oils were most compatible. Treatment of the plasticizers with molecular sieves or by passing through a column of silica gel improved the compatibility. The incompatibility of the curing agents and the plasticizers affected both the mechanical behavior of binders and propellants and the gel fraction of toluene swollen binders. The low temperature properties of the binders were not adequate for solid propellants useful at low temperatures although the glass transition temperatures of the binders were lower than -100°F. Carbon tetrachloride and tetrahydrofuran gave the maximum swelling ratios with the "workhorse" binder.

(C) The compatibility of the prepolymer and model compounds with beryllium, beryllium hydride and aluminum hydride was determined. The most difficulty involved aluminum hydride and phenyl isocyanate, a model compound, for the curing agent. Binders containing aluminum hydride gassed. Thermodynamic calculations of the expected performance of hydroxylammonium perchlorate, aluminum, "workhorse" binder systems were made.

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GLOSSARY OF TERMS

ADN	Adiponitrile
Ansul Ether 181	Tetraethylene glycol dimethyl ether
BDNPA	Bis-(2,2-dinitropropyl)-acetal
BDNPF	Bis-(2,2-dinitropropyl)-formal
Butarez CTL	Carboxy-terminated polybutadiene product of the Phillip's Petroleum Company
C-1	N,N-di-(2-cyanoethyl)-2,3-dihydroxy-propylamine
CED	Cohesive Energy Density
Citroflex A2	Triethyl acetylcitrate, product of C. Pfizer Co., Inc.
CTI	Triisocyanate, proprietary item of the Aerojet-General Corporation
DEA	Diethanolamine
DOZ	Dioctyl azelate
Dri - Na	Sodium-lead alloy, product of the J. T. Baker Chemical Co.
DTA	Differential thermal analysis
E_o	Initial uniaxial modulus
FeAA	Ferric acetylacetonate
GLC	Gas-liquid chromatography
HAP	Hydroxylammonium perchlorate
HC-434	Carboxy-terminated polybutadiene, product of Thiokol Chemical Corporation
HDI	Hexamethylene diisocyanate
Hycar CTB	Carboxy-terminated polybutadiene, product of B. F. Goodrich Chemical Company, see Table 10

IDP	Isodecyl Pelargonate, product of Emery Industries, Inc.
IR	Infrared
I_s	Specific Impulse
Light Circo Oil	General purpose naphthenic type softener for neoprene and natural rubber, product of the Sun Oil Co.
MS	Molecular sieve, 4A, product of the Linde Co.
MW	Molecular weight
NEMNC	2-Nitratoethyl N-nitro-N-methylcarbamate
Niax D-22	Dibutyltin dilaurate, product of the Union Carbide Co.
NMR	Nuclear magnetic resonance spectroscopy
Nujol	Mineral oil (registered trade name), product of Plough, Inc.
Oronite-6	Liquid polyisobutylene, product of the California Chemical Co.
S-141	Octyl diphenyl phosphate, product of the Monsanto Chemical Co.
S_{nb}	Nominal uniaxial break tensile stress
S_{nm}	Nominal maximum uniaxial tensile stress
Telagen CT	Carboxy-terminated polybutadiene, product of The General Tire and Rubber Co.
Telagen S	Functionally-terminated hydrogenated polybutadiene, product of The General Tire and Rubber Co.
T_G	Glass transition temperature
TMETN	Trimethylolethane trinitrate, 1,1,1-tri-(nitratomethyl)-ethane
VPO	Vapor phase osmometer
γ_b	Uniaxial strain at break
γ_m	Maximum uniaxial strain

GLOSSARY OF TERMS (Cont)

η	Viscosity, specifically for slurries
η_o	Viscosity, specifically for liquids
η_r	Relative viscosity, ratio of η to η_o
ϕ	Volume fraction
ϕ_f	Maximum volume fraction

(U) THE DEVELOPMENT AND EVALUATION OF A HYDROCARBON BINDER FOR HIGH ENERGY SOLID PROPELLANTS

I. (U) INTRODUCTION

This the first Quarterly Technical Report submitted in partial fulfillment of the requirements of Contract AF 04(611)-11419. The report covers the period 14 March through 13 June 1966.

II. (U) OBJECTIVE

The objective of this program is to further develop and evaluate a solid propellant binder system specifically to meet the most rigid demands of advanced, high performance solid rocket motors. The solid propellant binder system consists of an isocyanate-cured, saturated hydrocarbon prepolymer developed and evaluated under Contract AF 04(611)-10366. Further development and evaluation will involve propellant optimization, maximizing solids loading, adaptation to advanced oxidizers and fuels, and study of the environmental stability of the propellant.

III. (C) SUMMARY

The following is a summary of the accomplishments made during this reporting interval.

A. (U) The candidate prepolymer is now available commercially from The General Tire and Rubber Company under the registered trade name Telagen S. The Telagen S can be obtained with carboxy, primary hydroxy or secondary hydroxy terminal groups.

B. (U) A sample of Telagen S was separated on a column of 40A permeability limit polystyrene gel and both a molecular weight and functionality distribution derived. The functionality of the Telagen S did not vary with the molecular weight.

C. (U) A sample of CTI has been successfully stored for 6 months with only a 1.3% change in equivalent weight. Recrystallization is better than distillation for purification of CTI.

D. (U) NH_4ClO_4 stored on the shelf for as long as one year did not cause the loss of isocyanate functionality from a model curing agent in contact with it for 6 days at room temperature.

E. (U) A number of commonly used, commercially available plasticizers caused an appreciable loss of isocyanate functionality from curing agents dissolved in the plasticizer. Hydrocarbons, such as Nujol, Oronite-6, and Light Circo Oil, interfered least with the isocyanates.

F. (U) Plasticizers dried over 4A molecular sieves or passed through a column of silica gel were more compatible with the curing agent. Infrared analysis indicate that water is not the only impurity causing the interference.

G. (U) The effect of plasticizers on the mechanical behavior of binders shows the influence of the plasticizer-curing agent interaction. The plasticizing effect of a compound (as differentiated from its effect on curing reactions) is very difficult to establish, but some conclusions regarding the plasticizing merits of a compound may be made by using both mechanical behavior data and crosslink density information.

H. (U) While unplasticized binders give the best properties with an NCO to OH ratio of 1.00, a ratio of 1.05 is better for the plasticized systems.

I. (U) The Mooney-Rivlin C_1 constant of plasticized propellants is sensitive to the cure interference of the plasticizer. The C_1 constant varies linearly with the volume fraction of binder (or plasticizer) for IDP plasticized binders.

J. (U) The low temperature uniaxial tensile behavior of Telagen S-CTI-HDI binders is not adequate for preparation of solid propellants designed to operate at -75°F. The glass transition temperatures of binders containing typical plasticizers are below -100°F.

K. (U) Swelling of Telagen S binders has been a very useful tool for determining the effect of plasticizers on the curing reactions. Correlations have been made of the gel fractions of toluene swollen binders with the Mooney-Rivlin C_1 constants, with the maximum uniaxial tensile strengths, with the initial uniaxial modulus, and with the plasticizer-curing agent interaction.

L. (U) Propellant studies confirm the effect of plasticizers on the curing reactions and the beneficial effect of plasticizer pretreatment on the propellant properties.

M. (U) Replacement of DEA with C-1 in the candidate solid propellant changes the mechanical behavior radically. This leads to the conclusion that the DEA contributes to the crosslinking in these propellants while C-1 does not. Both agents are intended to reinforce the binder around the oxidizer particles.

N. (U) Aging of some plasticized propellant at 180°F for as long as 7 weeks showed little or no degradation except for one propellant plasticized with DOZ. These results are not definitive but were intended only for screening.

O. (U) The swelling of Telagen S binders was investigated in 13 solvents ranging in cohesive energy density from 52 to 160. The maximum swelling-CED curve showed peaks at 73.6 (carbon tetrachloride) and at 86.8 (tetrahydrofuran).

P. (U) The relative viscosities of NH_4ClO_4 -Oronite 6 slurries have been determined with NH_4ClO_4 ranging in particle size from 3-9μ, 43-104μ, 104-250μ, and 250-495μ. The data were fitted to the Eilers equation and the maximum solids loading for each particle size blend determined. The maximum range for 0.43 to 0.63 volume fraction of solids for the finest to the coarsest blend.

Q. (U) Model compounds were utilized to determine the compatibility of carboxy and hydroxy terminated Telagen S with Be and LMH-1. Similar tests were made with model curing agents. Confirmatory tests with Telagen S were also made.

R. (U) 2-Octanol and 1-decanol, models for the candidate prepolymer, were compatible with LMH-1 and passivated Be, no change of concentration or new peaks being detected by GLC. The model olefin, 1,7-octadiene, showed about 3% decrease in concentration but no new peak after 18 hours at 50°C on the same fuels. The model acids reacted with LMH-1 at 50°C; the extent of reaction being greater with a primary carboxylic acid and with freshly ground fuel.

S. (U) Pheryl isocyanate, a model curing agent, showed loss of functionality with both LMH-1 and Be after 18 hours at 50°C. Gas was evolved with LMH-1 but no new compounds were detected by GLC for either fuel.

T. (U) Hydroxy terminated Telagen S showed no adverse effects in the presence of chrome coated Be, LMH-1 or LMH-2. Binders containing LMH-1 gassed.

U. (C) Thermodynamic calculations were made for hydroxylammonium perchlorate (HAP) and aluminum in both the candidate binder system and a similar but unsaturated binder system. The unsaturated system shows a small advantage in specific impulse.

IV. TECHNICAL PROGRESS

A. (U) MATERIALS

1. Saturated Hydrocarbon Prepolymer

The work reported in this Quarterly Progress Report was done with the prepolymer developed under Contract AF 04(611)-10386. The prepolymer was made by The General Tire and Rubber Company according to the tentative requirements in Table 1.[1]

Table 1

(U) CHARACTERISTICS OF CANDIDATE PREPOLYMER (TELAGEN S)

Backbone	Saturated polybutadiene with about 35% 1,2-addition
Functional Groups	Secondary-OH
Molecular Weight	About 1500
Functionality	As close to 2 as possible
Viscosity	Less than 100 poises at 50°C

Twenty pounds of this candidate prepolymer were prepared under Contract AF 04(611)-10386. The remainder has been used to do the work reported here. The properties of this prepolymer are shown in Table 2.

Additional saturated prepolymers, both with carboxy and hydroxy functional groups, have been ordered for this project. The General Tire and Rubber Company is now supplying these prepolymers commercially under the registered trade name Telagen S.

---

(1) D. E. Johnson and A. J. Di Milo, "The Development and Evaluation of a Hydrocarbon Binder for High Energy Solid Propellants", Report No. AFRPL-TR-66-40, Aerojet-General Corporation, Sacramento, California, Contract AF 04(611)-10386, February 1966.

Table 2

(U) PROPERTIES OF SATURATED AND UNSATURATED HYDROXY-TERMINATED CANDIDATE PREPOLYMER (TELAGEN S)

	Unsaturated	Saturated
Molecular Weight		
Thecretical	1766	-
Solution Viscosity	1800	-
VPO	1620	1676[a]
Hydroxyl, meq/g	1.049	1.020
Functicnality[b]	1.70	1.71
Unsaturation, mm/g	17.1	0.28
cis	27.6	-
trans	38.3	-
vinyl	34.1	-
·sh, %	-	0.03
Antioxidant 2246, % added	0.5	-
Brookfield Viscosity, Poise at 25°C	28	190
Volatiles, %	-	0.1

[a]Estimated from VPO molecular weight of the prepolymer and change in unsaturation.

[b]Ratio of VPO molecular to equivalent weight.

B. (U) PHASE I

1. Introduction

Phase I involves a study of the exact cure stoichiometry of the prepolymer, the effects of various plasticizers on propellant properties, and the maximum achievable solids loading with NH_4ClO_4 and aluminum. The propellant with the highest specific impulse will be completely characterized with respect to mechanical behavior and will be evaluated ballistically at the 1-lb level. The specifications of the prepolymer will be established.

2. Prepolymer Characterization

A sample of Telagen S (Table 2) was fractionated on a 40A-permeability-limit polystyrene gel column. Average number molecular weight by Vapor Phase Osmometry and equivalent weight by Nuclear Magnetic Resonance Spectrometry were established for each fraction. The results are shown in Table 3. The two results marked with an asterisk may be considered doubtful since the fraction weights were inadequate for accurate analysis by the present procedure.

Table 3

(U) MOLECULAR WEIGHT AND FUNCTIONALITY DISTRIBUTION[a] OF TELAGEN S[b]

Fraction	Eq. Wt.[c]	Mol. Wt.[d]	Functionality	Fraction Wt.	% of Total
1	915*	2050	2.2	0.0915	6.0
2	1143	1678	1.5	0.4321	28.3
3	1021	1607	1.6	0.4802	31.5
4	888	1507	1.7	0.3136	20.6
5	884	1430	1.6	0.1769	11.6
6	321*	920	2.9	0.0313	2.0

Table 3 (Cont)

Average	MW from fractions	1606
	MW on neat material	1622
	Functionality (neat material)	1.66
	Functionality (from fractions)	1.65

---

[a]Gel permeation chromatographic separation recovery 99.33%.

[b]See Table 2.

[c]By NMR analysis of end groups.

[d]By VPO

If one neglects the doubtful values, the functionality does not vary with the molecular weight of the prepolymer. Typically an unsaturated polybutadiene shows an increase in functionality with molecular weight (Figure 1). This difference between polybutadienes and Telagen S may be due to the saturated nature of the latter which cannot be oxidatively polymerized to give a higher molecular weight, higher functionality material or it may be due to the narrower molecular weight range of Telagen S which does not allow the increase of functionality with molecular weight to be detected.

The current determination of the functionality of the prepolymer agrees with the determination made under Contract AF 04(611)-10386 and shown in Table 2.

3. Characterization of CTI

At the beginning of the present program, the isocyanate curing agents were analyzed again. An old sample of CTI had an equivalent weight of 76 compared to the previous value of 75. This material had been stored under argon at room temperature for 6 months, showing that it can be stored successfully.

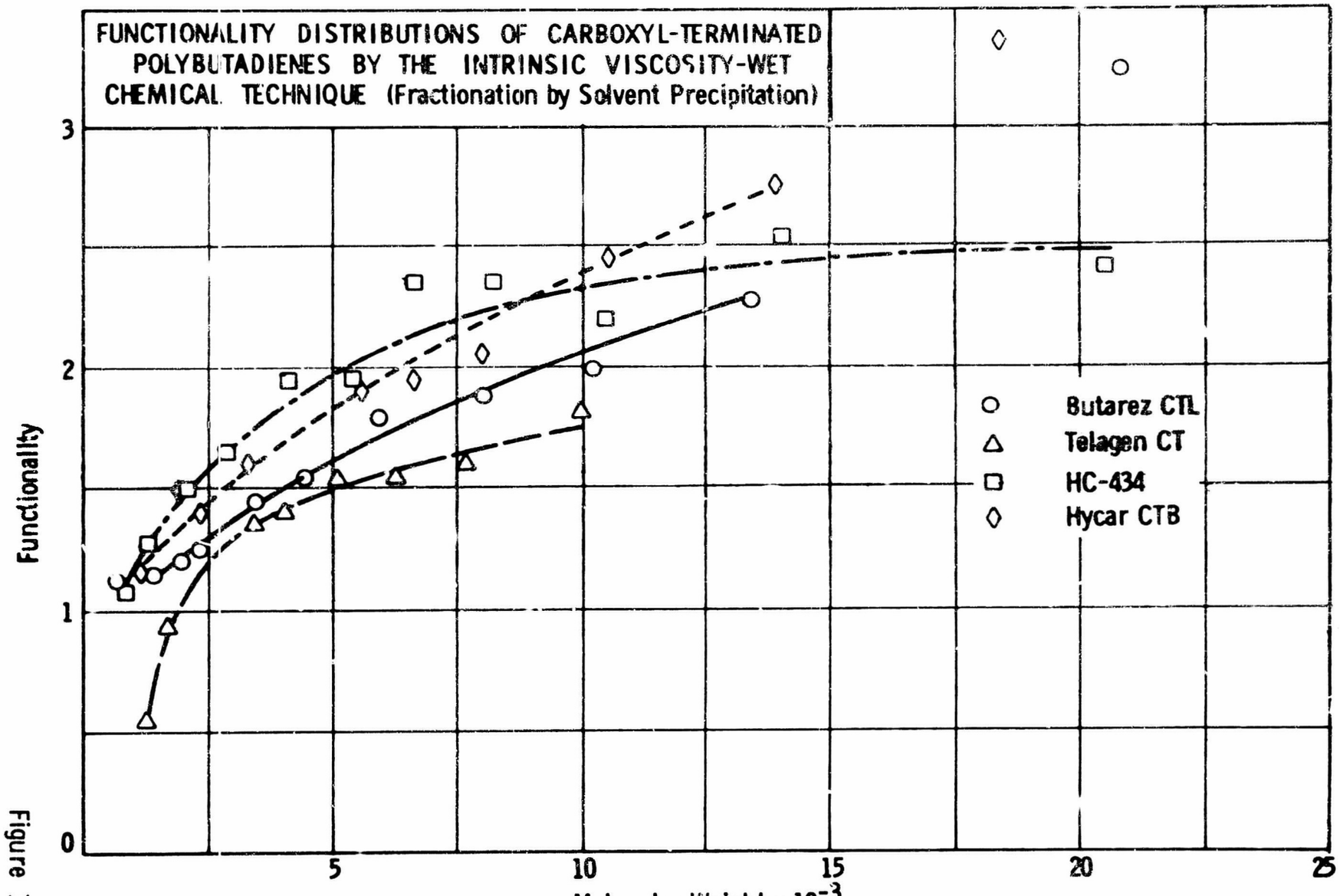
FUNCTIONALITY DISTRIBUTIONS OF CARBOXYL-TERMINATED POLYBUTADIENES BY THE INTRINSIC VISCOSITY-WET CHEMICAL TECHNIQUE (Fractionation by Solvent Precipitation)
Functionality
Molecular Weight x 10^{-3}
0
1
2
3
5
10
15
20
25
Butarez CTL
Telagen CT
HC-434
Hycar CTB

Figure 1

Another batch of CTI was prepared. After redistillation, the product had an assay of 86% (equivalent weight, 80.5), and on recrystallization, the assay increased to 97% (equivalent weight = 71.3). The results indicate that recrystallization is the preferred method for purifying CTI.

4. Effect of NH_4ClO_4 On Isocyanate Curing Agents

Phenyl isocyanate in toluene was used to determine the effect of NH_4ClO_4 on the isocyanate curing agents. Some of the NH_4ClO_4 samples were fresh and other had been stored on the shelf for 1 year. The particle sizes were 405μ and 10μ. None of the samples showed an isocyanate loss greater than the control after 6 days at room temperature. The conclusion is that NH_4ClO_4 would have a negligible effect on the isocyanate curing agents during the time necessary to cure a propellant.

5. Plasticizer Studies

a. Effect of Plasticizers on Curing Agents

The effect of the plasticizers on the curing agents was determined by preparing vials, each containing a plasticizer (5 gm), HDI or phenyl isocyanate (0.5 gm) and a drop of catalyst (Niax D-22 or 0.5 gm FeAA in 10 ml toluene). The disappearance of the isocyanate was followed by the usual titration methods. A summary of the results is shown on Tables 4 and 5. The isocyanate remaining (%; Tables 4 and 5) has been designated the plasticizer-curing agent interaction, but it must be noted that the magnitude of the interaction varies inversely with this figure, i.e., the higher the figure the lower the interaction.

Table 4

(U) EFFECT OF PLASTICIZERS ON ISOCYANATE CURING AGENTS[a]

Plasticizer	Plasticizer[b] Dried	Isocyanate Remaining, % 5 days at room temp.
Toluene (Control)	yes	92.6
Nujol	yes	92.3
Oronite-6	yes	88.6
Light Circo Oil	yes	87.0
n-Undecyl Cyanide	no	84.4
IDP	no	76.2
DOZ	yes	74.8
Citroflex	no	70.7
Squalene	no	70.2
S-141	yes	68.4
Methyl Butylcarbamate	no	58.8
Tetraethylene Glycol Dimethyl Ether	no	51.0

[a]Test solution consisted of plasticizer (5 gm), HDI (0.5 gm), and Niax D-22 (1 drop).

[b]Plasticizers dried over Molecular Sieve 4A except toluene, which was distilled from sodium.

Table 5

(U) EFFECT OF PLASTICIZERS ON ISOCYANATE CURING AGENTS[a]

Plasticizer	Plasticizer[b] Dried	Isocyanate Remaining, % 18 hr at room temp.
Toluene (Control)	yes	101
Nujol	yes	99.4
Light Circo Oil	yes	98.6
DOZ	yes	96.0
IDP	no	94.0
Squalene	no	84.6
Tetraethylene Glycol Dimethyl Ether	no	74.2

[a]Test solution consisted of plasticizer (5 gm), HDI (0.5 gm), and FeAA.

[b]Plasticizers dried over Molecular Sieve 4A except toluene, which was distilled from sodium.

It was apparent that the plasticizers contained impurities or adulterants which could seriously disrupt the cure stoichiometry of a binder or a propellant. Since many of these plasticizers had been made especially for use in solid propellants and conformed to specifications consistent with this use, a further study of the problem was made.

Of the plasticizers studied, the saturated hydrocarbons (oils) caused the smallest loss of isocyanate. The commonly used plasticizers, DOZ and IDP, caused a large loss of isocyanate functionality, part of which could be attributed to the effect of the medium on dimerization or trimerization of the isocyanate.

IDP and squalene were each dried over "Dri Na", a sodium-lead alloy, and over 4A Molecular Sieve pellets. The plasticizer was decanted from the solids and the disappearance of isocyanate in each of the dried plasticizers was determined. A summary of the results is shown in Table 6.

The plasticizers dried over "Dri Na" had a haze in them, possibly a fine precipitate of products from the reaction of impurities with the sodium. These products could act as basic catalysts for the isocyanate-consuming reactions. This method of drying can not be a useful treatment of plasticizers, unless the haze-causing materials are subsequently removed.

Table 6

(U) EFFECT OF DRIED PLASTICIZERS ON ISOCYANATE CURING AGENTS[a]

Plasticizer	Drying Agent	Isocyanate Remaining, % 3 days at room temp.
IDP	Dri Na	86
	Molecular Sieve	92
Squalene	Dri Na	54
	Molecular Sieve	73

[a]Test solution consisted of plasticizer (5 gm), phenyl isocyanate (0.5 gm) and FeAA.

In further studies on IDP and squalene, both materials were passed through a column of silica gel and their effect on isocyanate loss determined (Table 7).

Table 7

(U) EFFECT OF PLASTICIZER TREATMENT[a] ON ISOCYANATE CURING AGENTS

Plasticizer	Treatment[a]	Isocyanate Remaining, % 16-18 hr at room temp.[c]
Toluene	none	100
	yes	99
IDP	none	94
	yes	98
Squalene	none	85
	yes	98

[a]Passed through a column of silica gel.

[b]Test solution consisted of plasticizer (5 gm), phenyl isocyanate (0.5 gm) and FeAA.

[c]Untreated samples tested after 18 hours; treated after 16 hours.

Large yellow bands which formed on the columns were eluted and studied by near infrared. The IR spectrum of "as received" IDP showed two peaks - probably water and hydroxyl containing material. The spectrum of the material eluted from the column showed a decrease of the water peak, but the other peak was increased (Figure 2). Both spectra were taken with the purified IDP in the reference cell. With squalene, a carboxyl peak, which could be an ester or an aldehyde, was found in the as received sample (Figure 3). No further attempts were made to identify these peaks.

COMPARISON OF INFRARED SPECTRA OF "AS RECEIVED" IDP AND IDP PURITIES (PURIFIED IDP IN REFERENCE CELL)

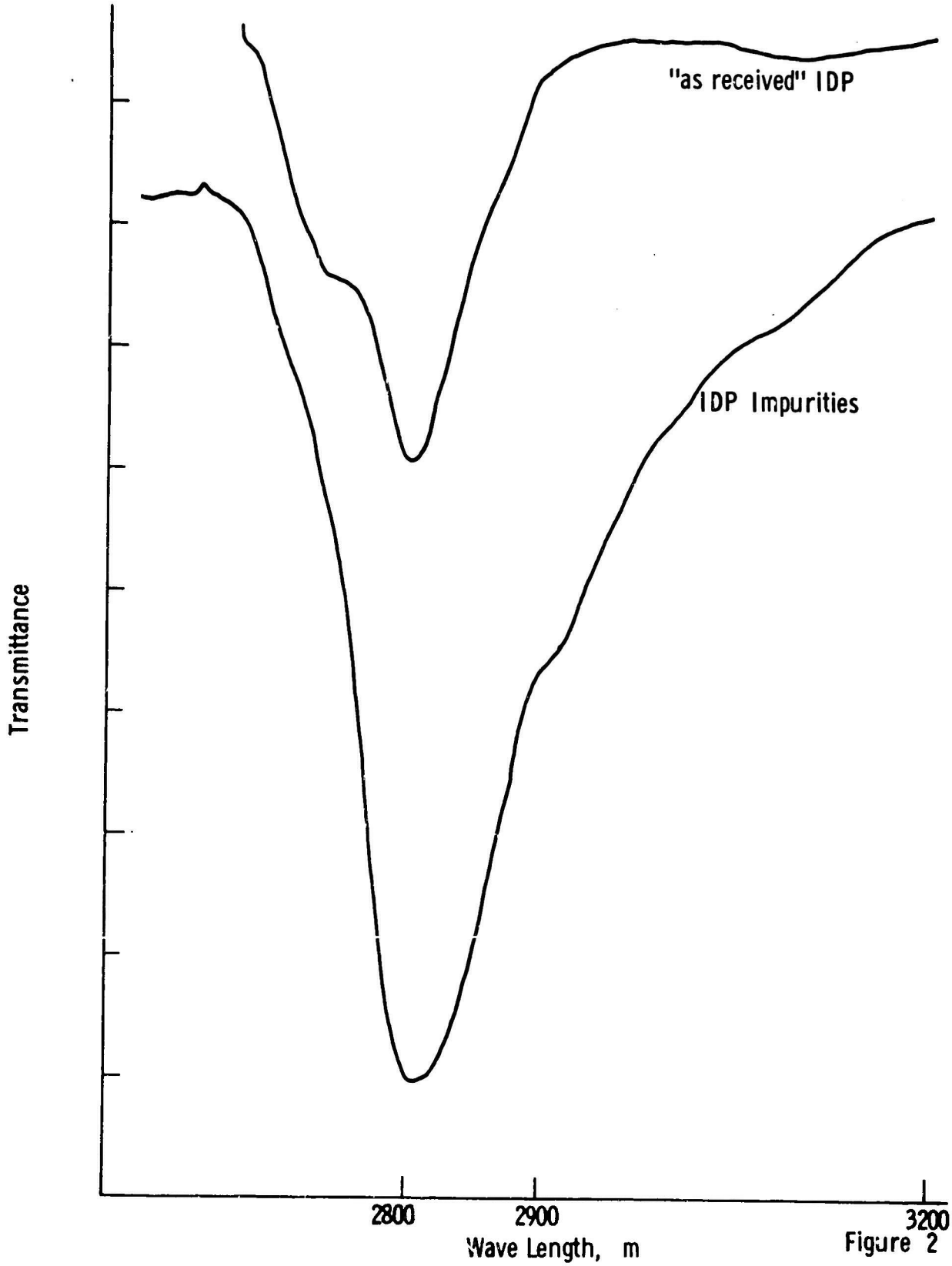

Figure 2

COMPARISON OF INFRARED SPECTRA OF "AS RECEIVED" SQUALENE AND PURIFIED SAMPLE

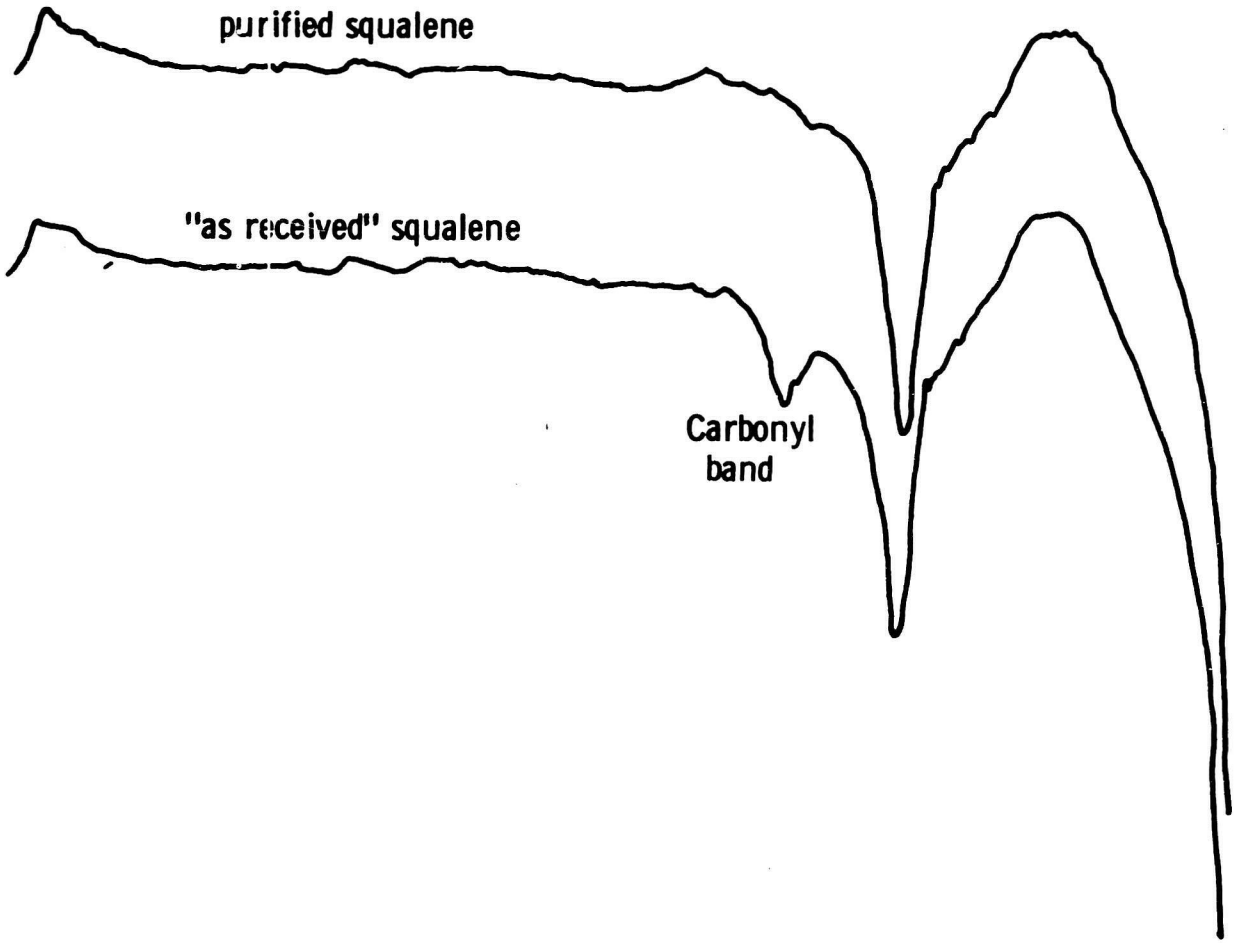

Figure 3

Tetraethylene glycol dimethyl ether (Ansul Ether 181) could not be purified on silica gel. In fact, the ether which was passed through silica gel caused a faster disappearance of isocyanate than the original (Table 8). Ansul Ether 181 (150 ml) was passed through a column of silica gel (100-200 mesh, 1 in. diam x 8 in.) and fractionated into eight cuts (each about 7.5 gm). The remainder was taken as one large fraction. The effect of the first and fifth fractions on the curing agent was compared with the effect of the unfractionated material (Table 8).

Table 8

(U) EFFECT OF ANSUL ETHER 181 ON ISOCYANATE CURING AGENTS[a]

Ansul Ether 181	Isocyanate Remaining, % 3 days at room temp
Untreated	53
Fractionated (Fraction 5)[b]	13.5
Fractionated (Fraction 1)[b]	0.7

[a] Test solution consisted of Ansul Ether (5 gm), phenyl isocyanate (0.5 gm), and FeAA.

[b] Ansul Ether fractionated into eight fractions and a residue by passage through a column of silica gel.

The unfractionated plasticizer caused less loss of phenyl isocyanate than the fractionated materials, but even the original plasticizer prevented the cure of the binders.

Squalene (Figure 3), and S-141 can be partially purified by passing them through a column of silica gel, but this treatment does not remove all of the impurities.

Silica gel will remove the yellow color from Oronite-6 and n-undecyl cyanide, but neither compound, the purified or "as received", showed any significant reduction of isocyanate assays over a period of 8 days. Work with binders confirms that these plasticizers do not interfere with the isocyanate reaction.

b. Effect of Plasticizers on Binder Properties

1) Introduction

Binders were prepared for the study of plasticizers and their effect on mechanical properties and glass transition temperatures.

While most of the binders were made at an NCO/OH ratio of 1.05, a 1.00 ratio was employed to determine effects of plasticizer on the cure stoichiometry. The use of a combination of mechanical properties and swelling data allows differentiation of binder-plasticizer interactions from the plasticizer-curing agent interactions which reduce the number of crosslinks. The mechanical properties of the plasticized binder are dependent upon both the plasticizing effect (binder-plasticizer interaction) and the effect on the cure reaction (curing agent-plasticizer interaction). On the other hand, the swelling behavior is dependent only on cure reaction, i.e., the number of crosslinks formed.

2) Mechanical Properties

Mechanical property data available to date have been summarized in Table 9. These data allow tentative conclusions concerning the effects of plasticizers and of stoichiometry on the properties of binders. Comparison of the mechanical properties, the tensile value, S_{mn}, especially, of binders without plasticizers and with NCO to OH ratios of 1.00 and 1.05 indicates a slightly better network with the 1.00 NCO to OH ratio.

Table 9

(U) EFFECT OF PLASTICIZERS AND STOICHIOMETRY ON THE
OF CANDIDATE BINDER[a] CURED AT 1

Reference No.	Plasticizer	% Wt.	Plasticizer Treatment[b]	Cure Time, Days	NCO:OH	S p
5	none	0.0	none	6	1.00	
8	IDP	20.0	none	6	1.00	
6	IDP	20.0	SiO_2	6	1.00	
17a	IDP	25.0	SiO_2	0.75	1.00	
17b	IDP	25.0	SiO_2	2	1.00	
17c	IDP	25.0	SiO_2	5	1.00	
17d	IDP	25.0	SiO_2	14	1.00	
1	none	0.0	none	7	1.05	
2	IDP	10.0	SiO_2	7	1.05	
3	IDP	20.0	SiO_2	7	1.05	
46-3	IDP	25.0	none	-	1.05	
4	IDP	30.0	SiO_2	7	1.05	
18a	DOZ	26.3	none	3	1.00	
18	DOZ	26.3	none	5	1.00	
19	DOZ	26.3	SiO_2	5	1.00	
17-2	DOZ	25.0	MS	10	1.05	
9	S-141	25.0	MS	6	1.00	
10	S-141	25.0	SiO_2	6	1.00	
17-3	S-141	25.0	MS	10	1.05	
14	Ether 181	25.0	none	6	1.00	
17-1	Oronite	25.0	MS	10	1.05	
20	Light Circo Oil	22.9	MS	5	1.00	
17-4	Light Circo Oil	25.0	none	10	1.05	
46-2	Nujol	25.0	MS	10	1.05	
46-1	Squalene	25.0	MS	10	1.05	
7	Squalene	25.0	SiO_2	6	1.05	
15	Undecyl Cyanide	25.0	none	3	1.00	
16	Undecyl Cyanide	25.0	SiO_2	3	1.00	

[a]Secondary hydroxy-terminated saturated hydrocarbon prepolymer cured with ~ 1 to 4 equival

[b]MS = contacted with Linde Molecular Sieve; SiO_2 = passed through column of silica gel.

Table 9

ASTICIZERS AND STOICHIOMETRY ON THE MECHANICAL BEHAVIOR OF CANDIDATE BINDER[a] CURED AT 135°F

Cure Time, Days	NCO:OH	Mechanical Properties				Mooney-Rivlin	
		S_{max} psi	γ_m %	γ_b %	E_o psi	C_1 kg/cm^2	C_2 kg/cm^2
6	1.00	74	478	478	69	0.23	0.57
6	1.00	30	510	- [c]	20	0.10	0.13
6	1.00	43	536	537	22	0.14	0.16
0.75	1.00	24	480	- [c]	14	-	-
2	1.00	22	440	440	16	-	-
5	1.00	26	450	450	19	-	-
14	1.00	30	476	476	19	-	-
7	1.05	65	358	358	72	0.28	0.57
7	1.05	3[illegible]	325	325	41	0.22	0.26
7	1.05	31	375	375	23	0.15	0.17
-	1.05	34	450	462	22	0.14	0.13
7	1.05	20	365	365	16	0.10	0.10
3	1.00	23	540	540	12	-	-
5	1.00	23	511	511	12	-	-
5	1.00	28	454	454	20	-	-
10	1.05	46	472	472	24	0.16	0.17
6	1.00	15	510	- [c]	13	0.05	0.11
6	1.00	20	510	- [c]	16	0.07	0.11
10	1.05	39	506	506	26	0.13	0.16
6	1.00	dissolved in toluene and trichloroethylene					
10	1.05	48	400	400	34	0.20	0.24
5	1.00	48	566	566	31	-	-
10	1.05	52	404	404	32	0.20	0.25
10	1.05	43	354	353	34	0.20	0.20
10	1.05	18	458	- [c]	11	0.08	0.06
6	1.05	23	520	- [c]	25	0.07	0.12
3	1.00	28	425	425	21	0.12	0.13
3	1.00	30	500	500	18	0.10	0.12

[b] repolymer cured with a 1 to 4 equivalent ratio of CTI and HDI.

passed through column of silica gel. [c] Bond failure or no break.

2

The table also indicates that binders plasticized with IDP or DOZ have better properties when the plasticizer is passed through a column of silica gel. The use of squalene or S-141 passed through silica gel also improves binder properties. The hydrocarbon plasticizers, Oronite, Light Circo Oil, and Nujol, gave the best properties.

The table demonstrates that those plasticizers which showed the greatest effect on the curing agents have a great effect on the mechanical properties. The effect is to degrade the mechanical behavior (lower break tensile and lower modulus). The mechanical properties are improved in some cases by treatment of the plasticizer.

There is a straight line relationship between the Mooney-Rivlin C_1 and volume fraction of binder for a series of binders with increasing amounts of IDP (Figure 4). The logarithm of the tensile or of the initial modulus versus volume fraction of plasticizer gave a linear relationship when plotted on semilog paper (Figure 5).

Table 10 below demonstrates the effect of some plasticizers (26 vol %) on the properties of binders.

Table 10

(U) EFFECT OF PLASTICIZERS[a] ON THE MECHANICAL PROPERTIES OF TELAGEN S-CTI-HDI BINDERS

Reference No.	Plasticizer[a]	σ_{nm} psi	γ_m %	γ_b %	σ_o psi
5	None	74	478	478	69
20	Light Circo Oil	48	566	566	31
19	DOZ	28	454	454	20
17C	IDP	26	450	450	19

[a]Data extracted from Table 9; plasticizer content 26 vol %.

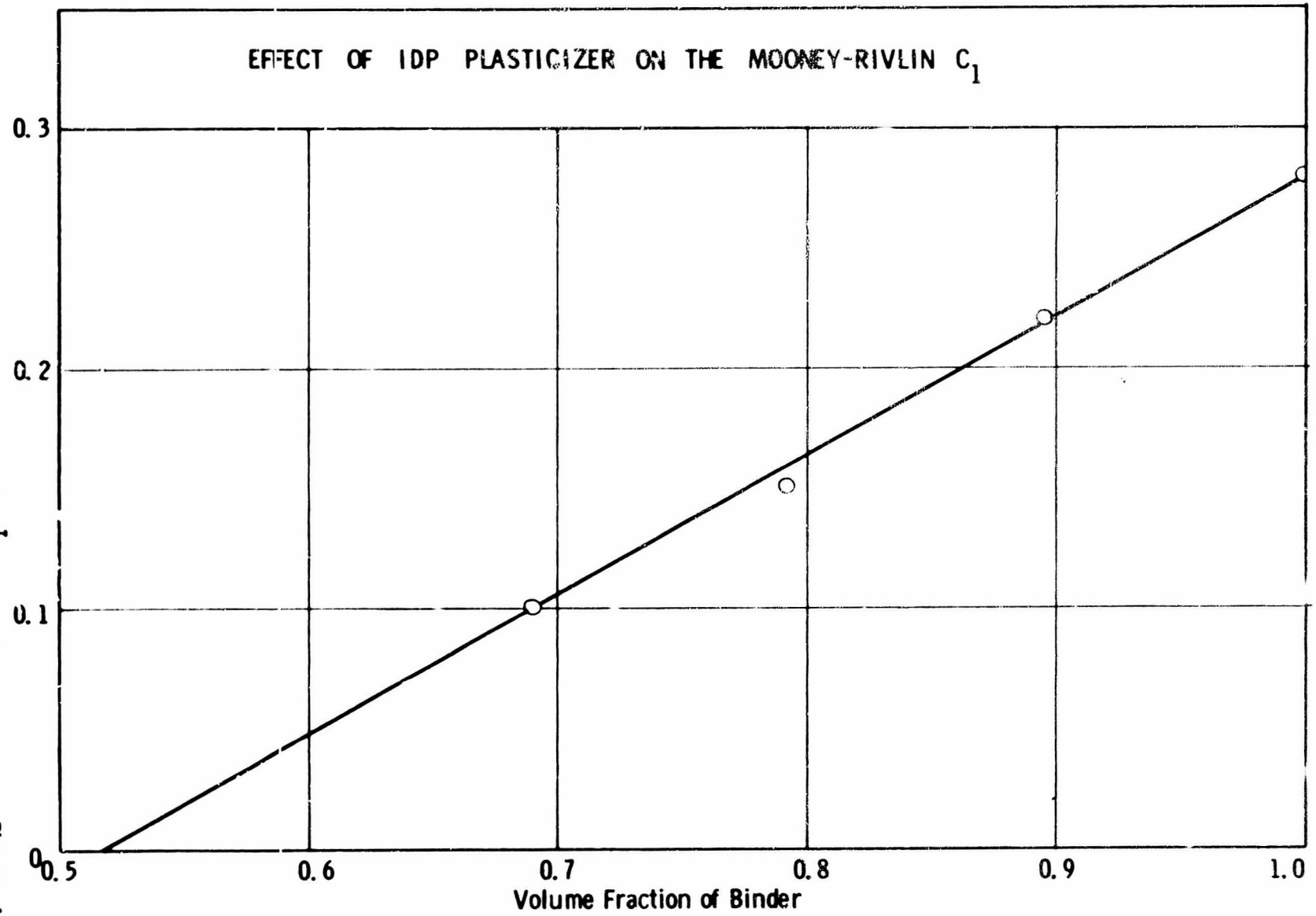
EFFECT OF IDP PLASTICIZER ON THE MOONEY-RIVLIN C_1
Mooney-Rivlin C_1, kg/cm^2
0.3
0.2
0.1
0
0.5
0.6
0.7
0.8
0.9
1.0
Volume Fraction of Binder

Figure 4

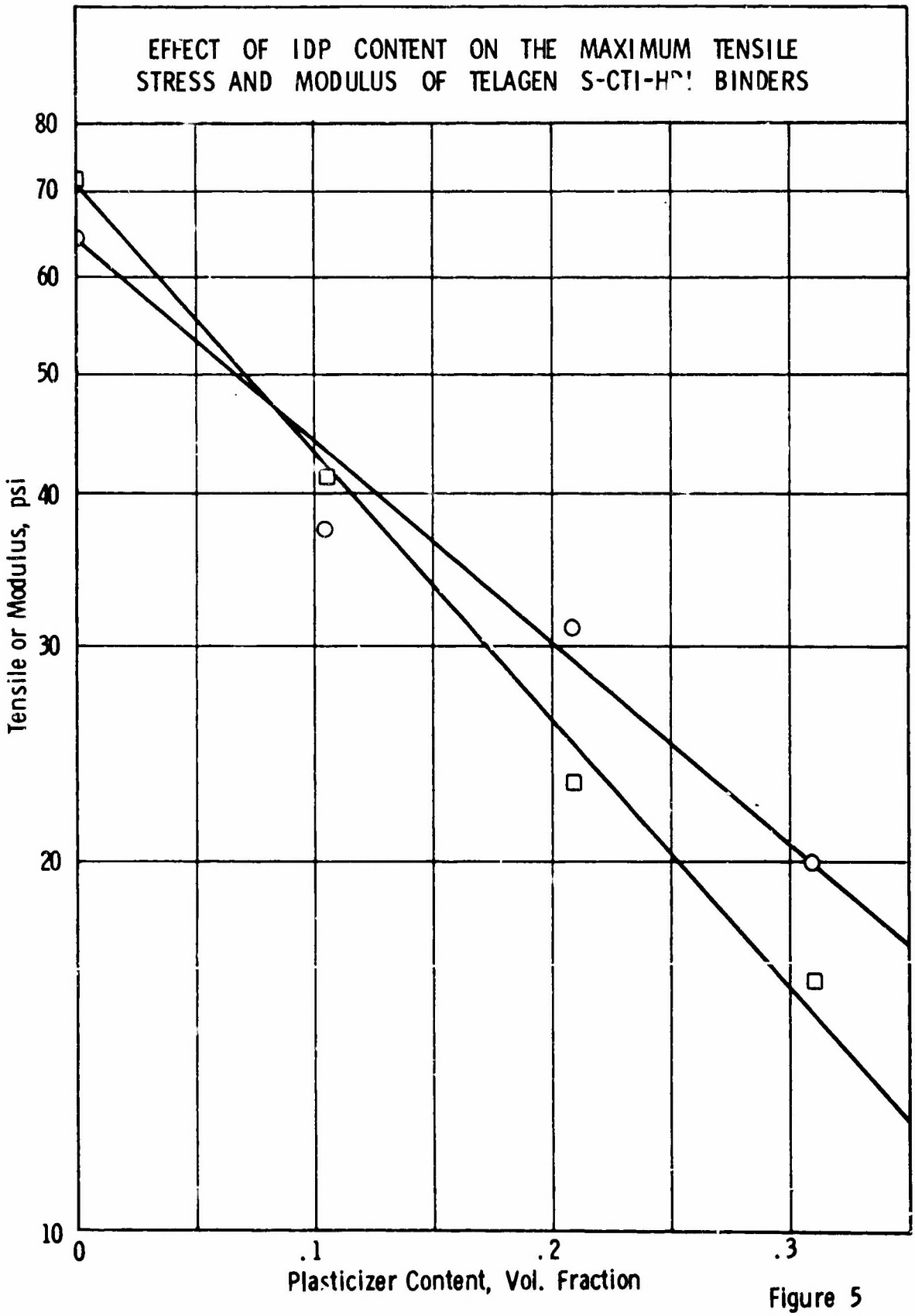
EFFECT OF IDP CONTENT ON THE MAXIMUM TENSILE STRESS AND MODULUS OF TELAGEN S-CTI-HT BINDERS
80
70
60
50
40
30
20
10
Tensile or Modulus, psi
0
.1
.2
.3
Plasticizer Content, Vol. Fraction

Figure 5

The plasticizers DOZ and IDP, which affect the curing agents have a much greater effect than the Light Circo Oil. The effect is, however, due in large measure to the decreased crosslink density caused by interference of the plasticizers with the curing reactions.

3) Low Temperature Mechanical Properties

Table 11 summarizes the low temperature properties of some plasticized binders. The results are complicated by the interference of some of the plasticizers with the cure reactions. None of the plasticizers give adequate low temperature properties. The plasticized binders all show glass transition temperatures below -100°F (Table 12).

4) Stress Relaxation of Plasticized Binders

The uniaxial stress relaxation properties of some plasticized binders at 77° and 150°F are shown in Table 13. The equilibrium moduli for the binder have been converted to equilibrium moduli for the networks (unplasticized system) by dividing the former by the cube root of the volume fraction of network.

The equilibrium moduli are higher for those plasticizers which affect the curing agents least. This is indicated in Figure 6.

The relaxation times are also shown, but these do not indicate any well defined trend.

Table 11

(U) EFFECT OF PLASTICIZERS ON LOW TEMPERATURE MECHANICAL PROPERTIES[a]

Reference No.	Plasticizer	Content Wt%	Mechanical Properties											
			77°F				-40°F				-75°F			
			S_m	γ_m	γ_b	E_o	S_m	γ_m	γ_b	E_o	S_m	γ_m	γ_b	E_o
17-2	DOZ	25	46	472	472	24	786	447	447	380	1000[b]	225[b]	225	1140
17-3	S-141	25	39	506	506	26	897	277	278	740	1490	165	165	1697
17-4	Light Circo Oil	25	52	404	404	32	936	270	271	880	2930	215	215	13380
17-1	Oronite	25	48	400	400	34	976	324	326	780	1161	187	187	1238
1	None	0	65	358	358	72	1805	192	192	3600	3570	6.7	176[c]	75000
2	IDP	10	37	325	325	41	749	266	266	930	3160	210	216	30500
3	IDP	20	31	375	375	23	440	317	317	410	1390	210	210	1250
4	IDP	30	20	365	365	16	340	440	440	270	1130	240-	246	990

[a] For more binder data see Table 9.

[b] Break at flaw.

[c] Yield point.

Table 12

(U) EFFECT OF PLASTICIZER ON T_G OF CANDIDATE BINDER

Plasticizer	Plasticizer (weight %)	T_G [c] °F
Oronite	25	-121
DOZ	25	-125
S-141	25	-121
Light Circo Oil	25	-112

Table 13

(U) STRESS RELAXATION PROPERTIES OF SOME PLASTICIZED BINDERS[a]

Reference No.	Plasticizer	Content vol %	Temp °F	Initial Modulus psi	Equilibrium Modulus, psi		Apparent τ [b] min	Recovery %
					Binder	Network		
17-3	S-141	21.7	77	25	16.1	17.4	284	94
			150	21	17.1	18.6	1520	94
17-2	DOZ	24.8	77	31	20.1	21.9	418	83
			150	21	19.9	21.7	1780	99
17-1	Oronite	26.5	77	30	23.2	25.7	340	94
			150	26	24.8	27.5	1075	97
17-4	Light Circo Oil	28.2	77	39	26.2	29.3	394	85
			150	30	27.0	30.1	743	97

[a] Binder data in Table 9.

[b] Relaxation time = time for tensile to be reduced to 1/2 of initial value.

[c] Network modulus = binder modulus /(bol fraction network)$^{1/3}$; stress relaxation determined at 25% elongation.

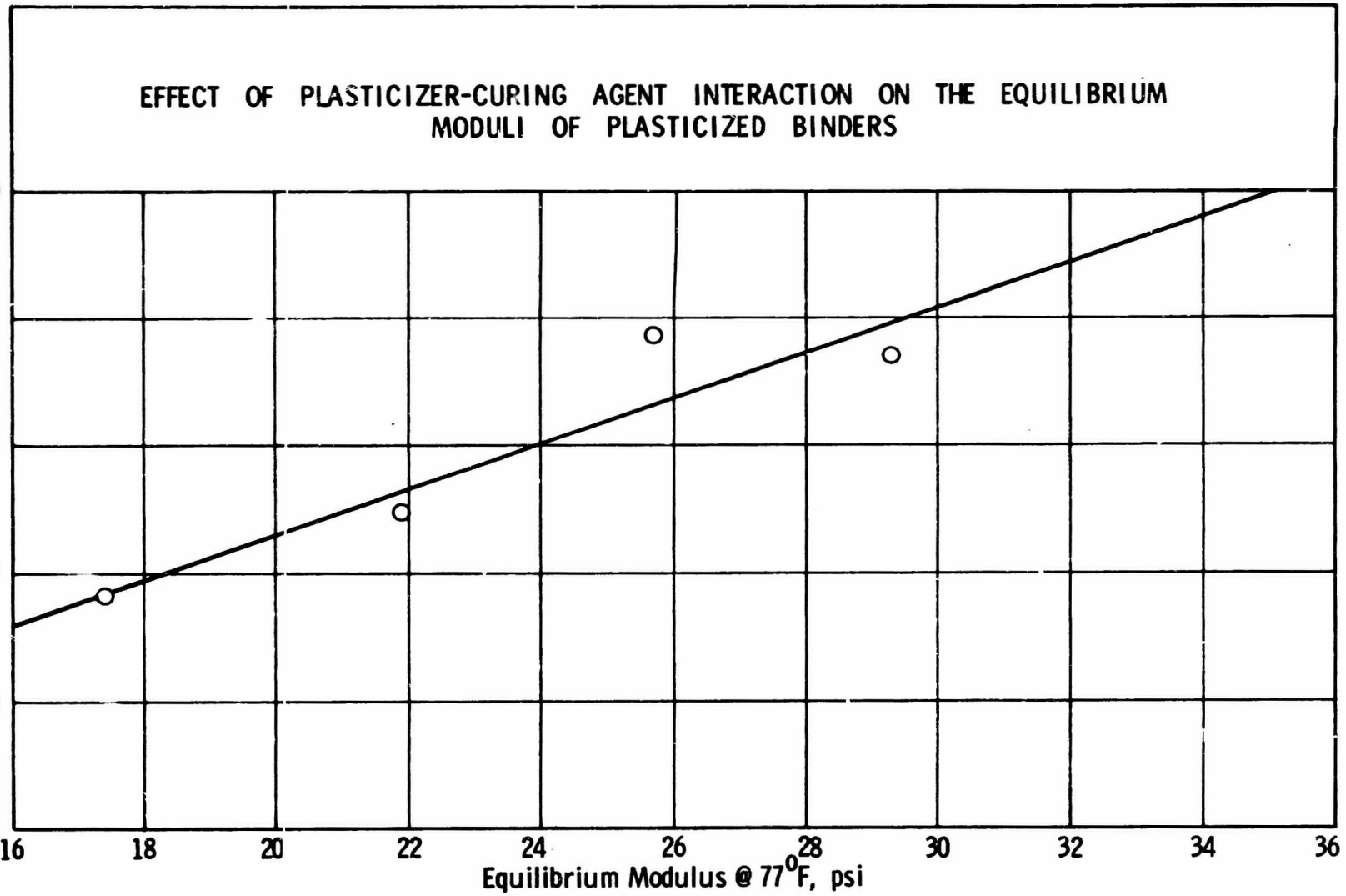
EFFECT OF PLASTICIZER-CURING AGENT INTERACTION ON THE EQUILIBRIUM MODULI OF PLASTICIZED BINDERS
Plasticizer-Curing Agent Interaction, %
100
90
80
70
60
50
16
18
20
22
24
26
28
30
32
34
36
Equilibrium Modulus @ 77°F, psi

Figure 6

5) Swelling of Plasticized Binders

Table 14 shows the effect of swelling of most of the binders listed in Table 9. The solvent is toluene. Again the effect of the plasticizers on the curing agents is very apparent. Table 15 and Figure 7 demonstrate the effect of plasticizer-curing agent interaction on gel fraction. As indicated in Table 15, there is also a qualitative relation between the effect of the plasticizer on the rate of the isocyanate reaction and the gel fraction.

That the change in mechanical properties on plasticization of a binder is not only the effect of plasticizer-binder interaction, is shown by other correlations with the gel fraction of swollen binders. Figure 8 shows the Mooney-Rivlin C_1 constant for the plasticized binders vs the gel fraction of the binder. This figure does not include the data for binders plasticized with n-undecyl cyanide.

Figures 9 and 10 relate the gel fraction to the maximum uniaxial tensile strength and to the initial uniaxial modulus of the binders. The tensile strength-gel fraction relation is very close to linear, and shows considerable scatter. The modulus-gel fraction relation has more curvature and shows less scatter.

Figures 11-16 show the effect of plasticizer content and treatment on the gel fraction of toluene swollen binders. Figures 11, 13 and 16 suggest that the gel fraction varies linearly with the plasticizer content. These figures also suggest that the IDP and DOZ passage through a column of silica gel is a more effective treatment than drying over molecular sieves. The hydrocarbon plasticizers, except squalene, are not much affected by treatment probably because they contain very little contaminants which interfere with cure. Squalene and S-141 are not greatly improved by treatment.

Table 14

(U) GEL AND SOL FRACTION FOR PLASTICIZED BINDERS[a]
(TELAGEN S-CTI-HDI) SWOLLEN IN TOLUENE

Reference No.	Plasticizer	Content Wt%	Treatment[b]	Time to Maximum Swelling, days	Gel Fraction	Sol Fraction
5	none	0.0	none	8	0.079	0.241
8	IDP	20.0	none	8	.054	.282
6	IDP	20.0	SiO_2	8	.063	.248
17a	IDP	25.0	SiO_2	-	.056	.346
17b	IDP	25.0	SiO_2	6	.058	.251
17c	IDP	25.0	SiO_2	6	.060	.241
1	none	0.0	none	6	.091	.228
2	IDP	10.0	SiO_2	6	.081	.258
3	IDP	20.0	SiO_2	8	.067	.234
46-3	IDP	25.0	none	-	.063	.296
4	IDP	30.0	SiO_2	8	.057	.251
18A	DOZ	26.3	none	-	.050	.37
18	DOZ	26.3	none	-	.051	.284
19	DOZ	26.3	SiO_2	-	.062	.224
17-2	DOZ	25.0	MS	9	.069	.245
9	S-141	25.0	MS	8	.041	.350
10	S-141	25.0	SiO_2	8	.050	.338
17-3	S-141	25.0	MS	9	.061	.293
14	Ether 181	25.0	none	-	dissolved	
17-1	Oronite	25.0	MS	6	.075	.188
20	Light Circo Oil	22.9	MS	-	.074	.219
17-4	Light Circo Oil	25.0	none	6	.073	.271
46-2	Nujol	25.0	MS	-	.081	.229
46-1	Squalene	25.0	MS	-	.042	.421
7	Squalene	25.0	SiO_2	8	.044	.373
15	n-Undecyl Cyanide	25.0	none	-	.074	.078
16	n-Undecyl Cyanide	25.0	SiO_2	-	.066	.107

[a] Binder data in Table 9.

[b] MS = contacted with Linde Molecular Sieves, SiO_2 = passed through column of silica gel.

Table 15

(U) EFFECT OF PLASTICIZER-CURING AGENT INTERACTION ON GEL FRACTION OF BINDERS

Plasticizer	Plasticizer-Curing Agent Interaction, %[a]	Rate of Isocyanate Reaction	Gel Fraction
None	none	-	0.091
Nujol	92.3	fast	0.081
Oronite	88.6	fast	.075
Light Circo Oil	87.0	fast	.073
IDP	76.2	moderate	.063
DOZ	74.8	moderate	.069
Squalene	70.2	no data	.042
S-141	68.4	no data	.061
Ether 181	51.0	slow	dissolves

[a] See Table 4; larger figures indicate smaller interaction.

Figures 11 and 13 indicate that IDP and DOZ have the same effect on the gel fraction of the plasticizer (they fall on the same line). While the number of data are small, they present the possibility that the reduction of gel fraction (or the crosslink density) of the binders by plasticizer may be due to a cause other than impurities which affect the cure reaction. It would be rather fortuitous for IDP and DOZ to have impurities of a type and content which would cause both plasticizers to affect the cure of Telagen S binders in the same manner.

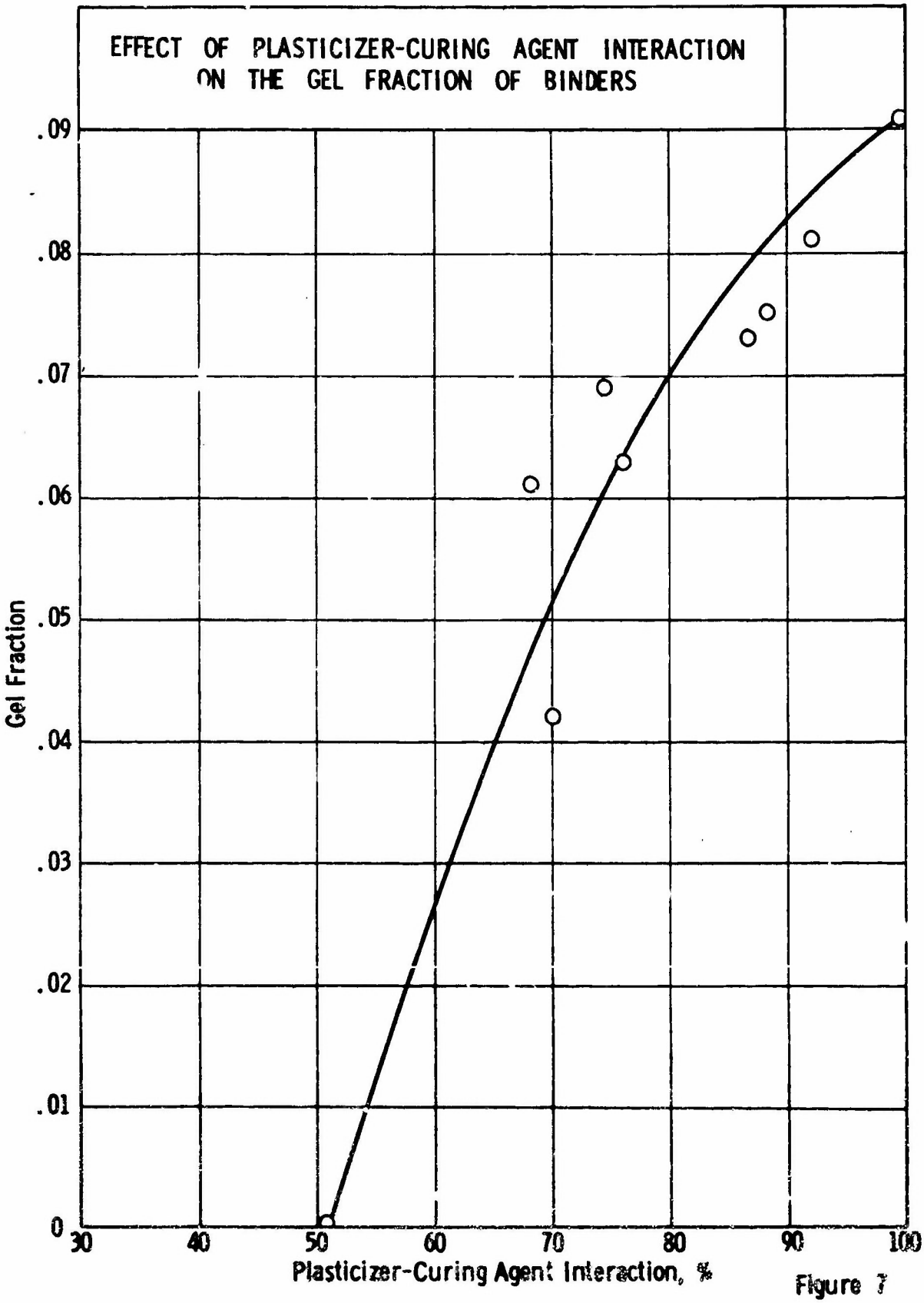
EFFECT OF PLASTICIZER-CURING AGENT INTERACTION ON THE GEL FRACTION OF BINDERS
Gel Fraction
.09
.08
.07
.06
.05
.04
.03
.02
.01
0
30
40
50
60
70
80
90
100
Plasticizer-Curing Agent Interaction, %

Figure 7

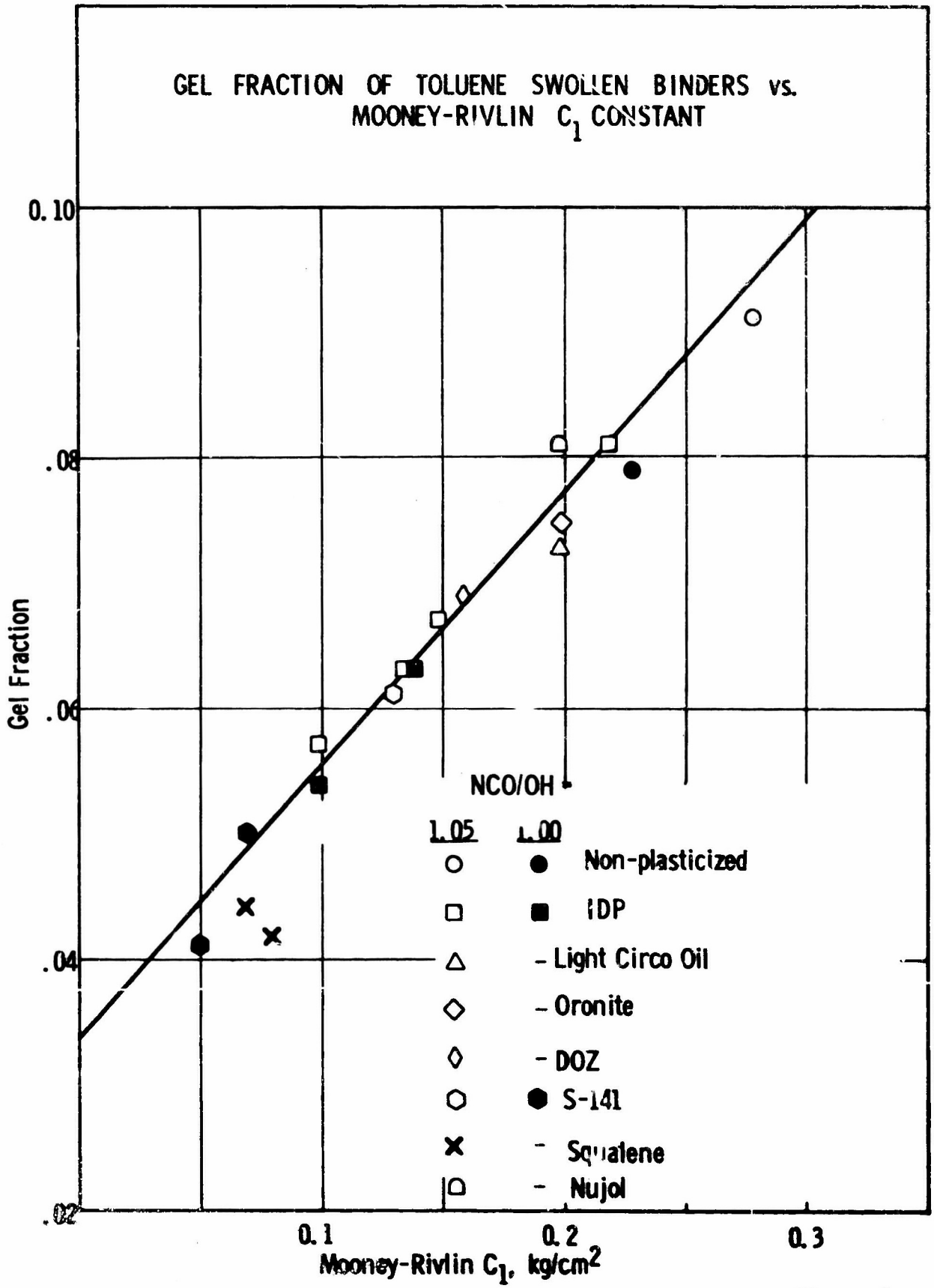
GEL FRACTION OF TOLUENE SWOLLEN BINDERS vs.
MOONEY-RIVLIN C_1 CONSTANT
0.10
.08
.06
.04
.02
Gel Fraction
NCO/OH
1.05
1.00
Non-plasticized
IDP
- Light Circo Oil
- Oronite
- DOZ
S-141
- Squalene
- Nujol
0.1
0.2
0.3
Mooney-Rivlin C_1, kg/cm^2

Figure 8

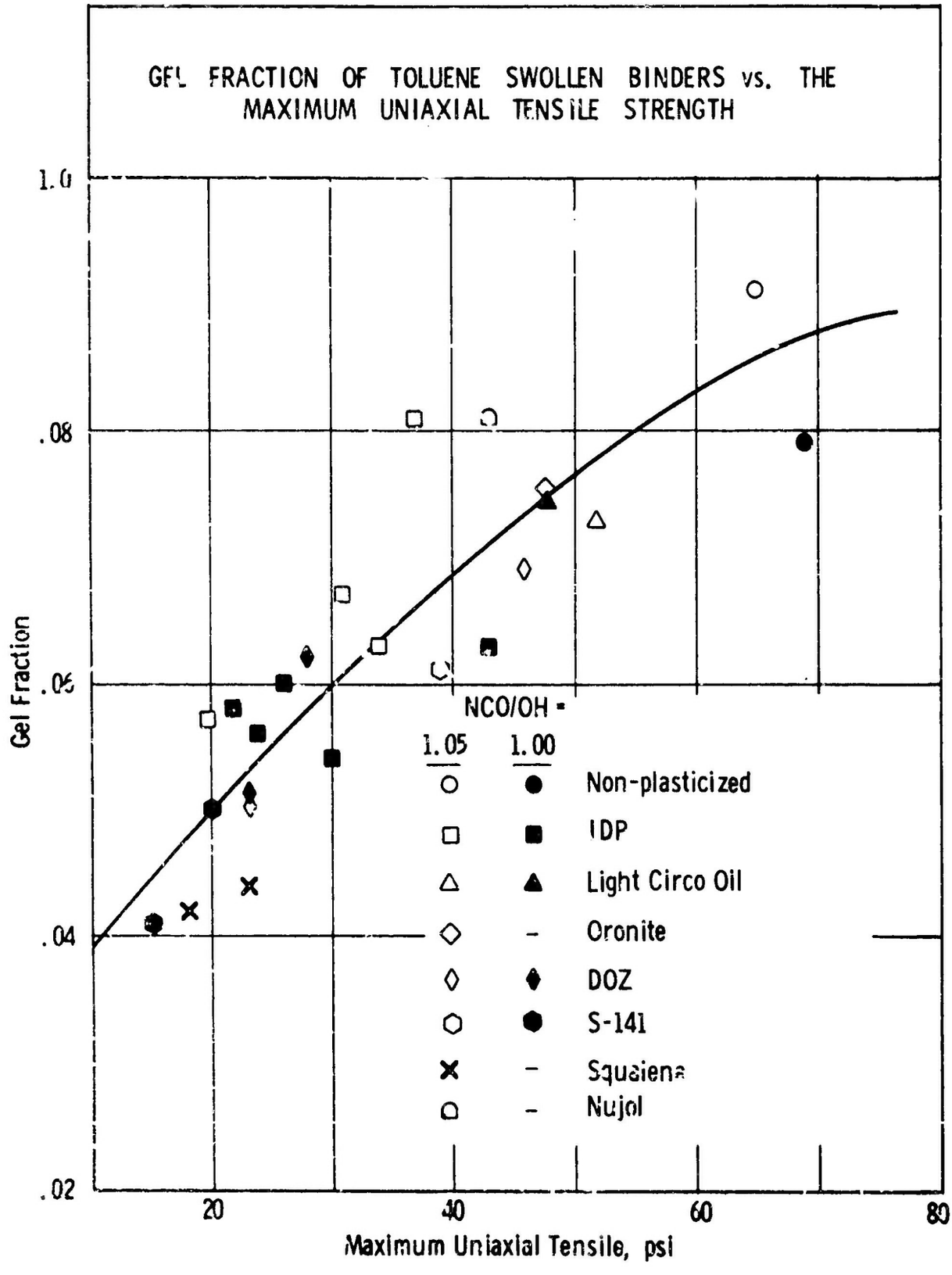
GEL FRACTION OF TOLUENE SWOLLEN BINDERS vs. THE MAXIMUM UNIAXIAL TENSILE STRENGTH
1.0
.08
.06
.04
.02
Gel Fraction
NCO/OH =
1.05
1.00
Non-plasticized
IDP
Light Circo Oil
Oronite
DOZ
S-141
Squalene
Nujol
20
40
60
80
Maximum Uniaxial Tensile, psi

Figure 9

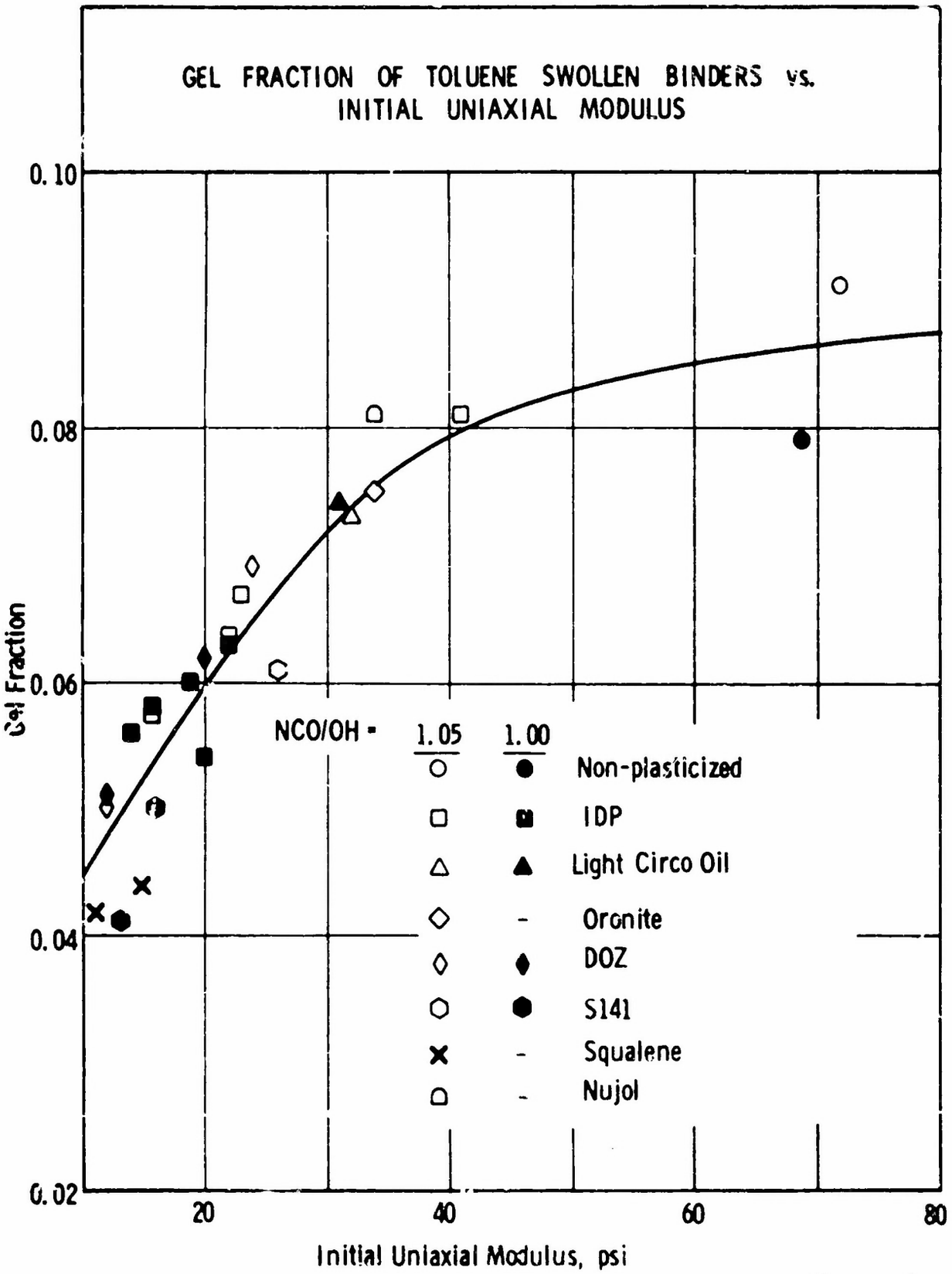
GEL FRACTION OF TOLUENE SWOLLEN BINDERS vs.
INITIAL UNIAXIAL MODULUS
0.10
0.08
0.06
0.04
0.02
Gel Fraction
20
40
60
80
Initial Uniaxial Modulus, psi
NCO/OH =
1.05
1.00
Non-plasticized
IDP
Light Circo Oil
Oronite
DOZ
S141
Squalene
Nujol

Figure 10

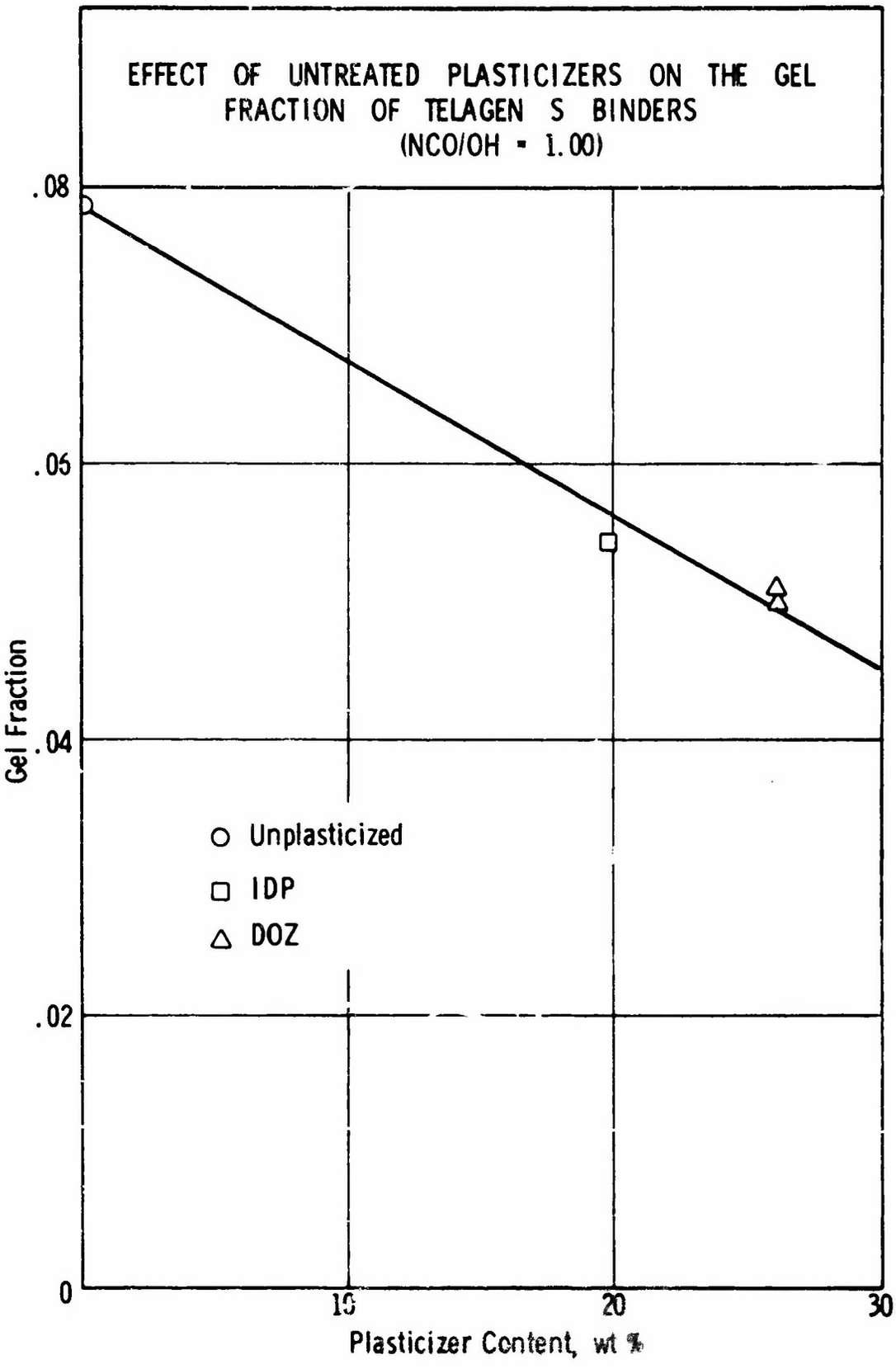
EFFECT OF UNTREATED PLASTICIZERS ON THE GEL FRACTION OF TELAGEN S BINDERS
(NCO/OH = 1.00)
.08
.06
.04
.02
0
Gel Fraction
Unplasticized
IDP
DOZ
10
20
30
Plasticizer Content, wt %

Figure 11

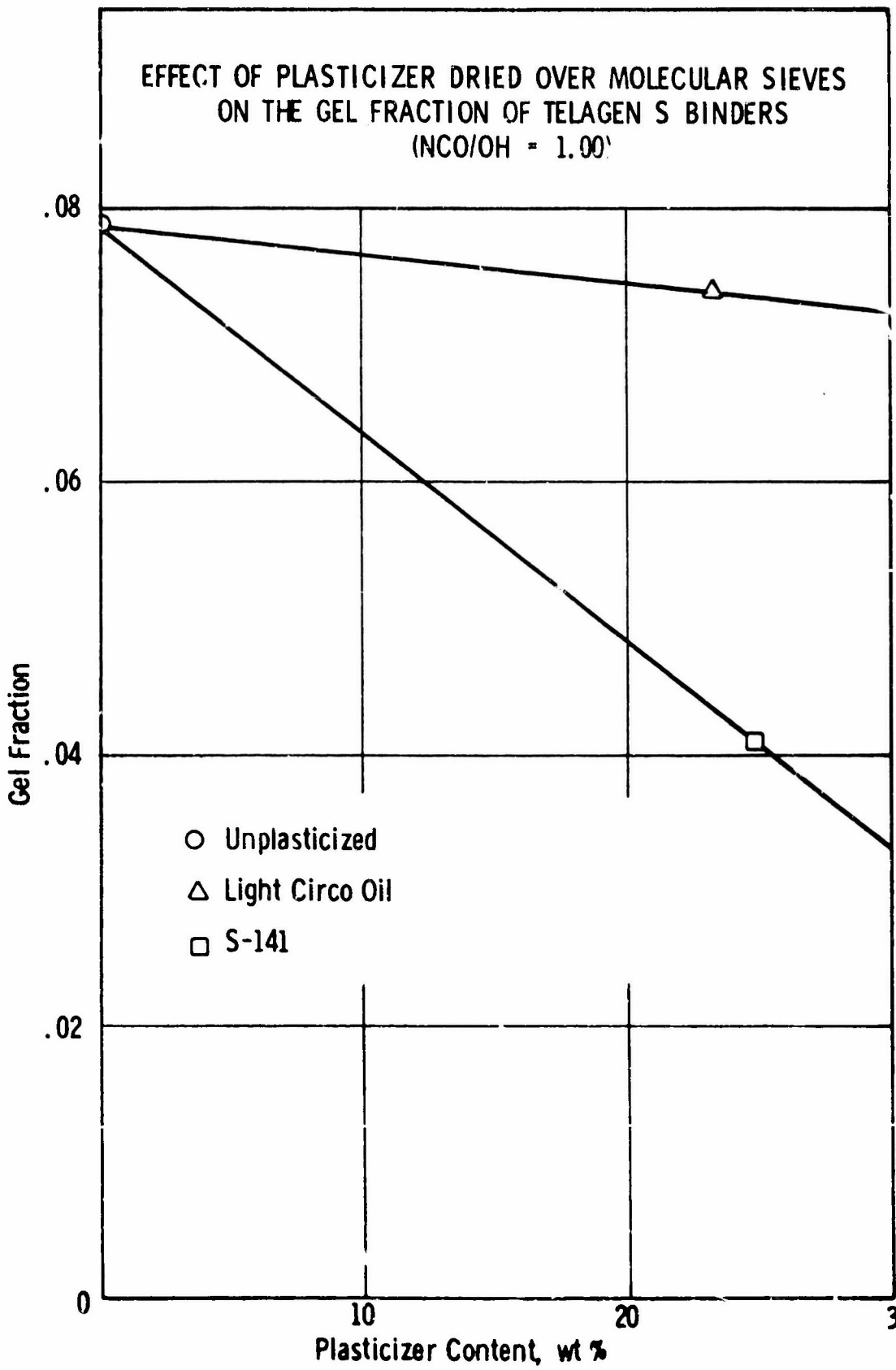
EFFECT OF PLASTICIZER DRIED OVER MOLECULAR SIEVES
ON THE GEL FRACTION OF TELAGEN S BINDERS
(NCO/OH = 1.00)
.08
.06
.04
.02
0
Gel Fraction
Unplasticized
Light Circo Oil
S-141
10
20
30
Plasticizer Content, wt %

Figure 12

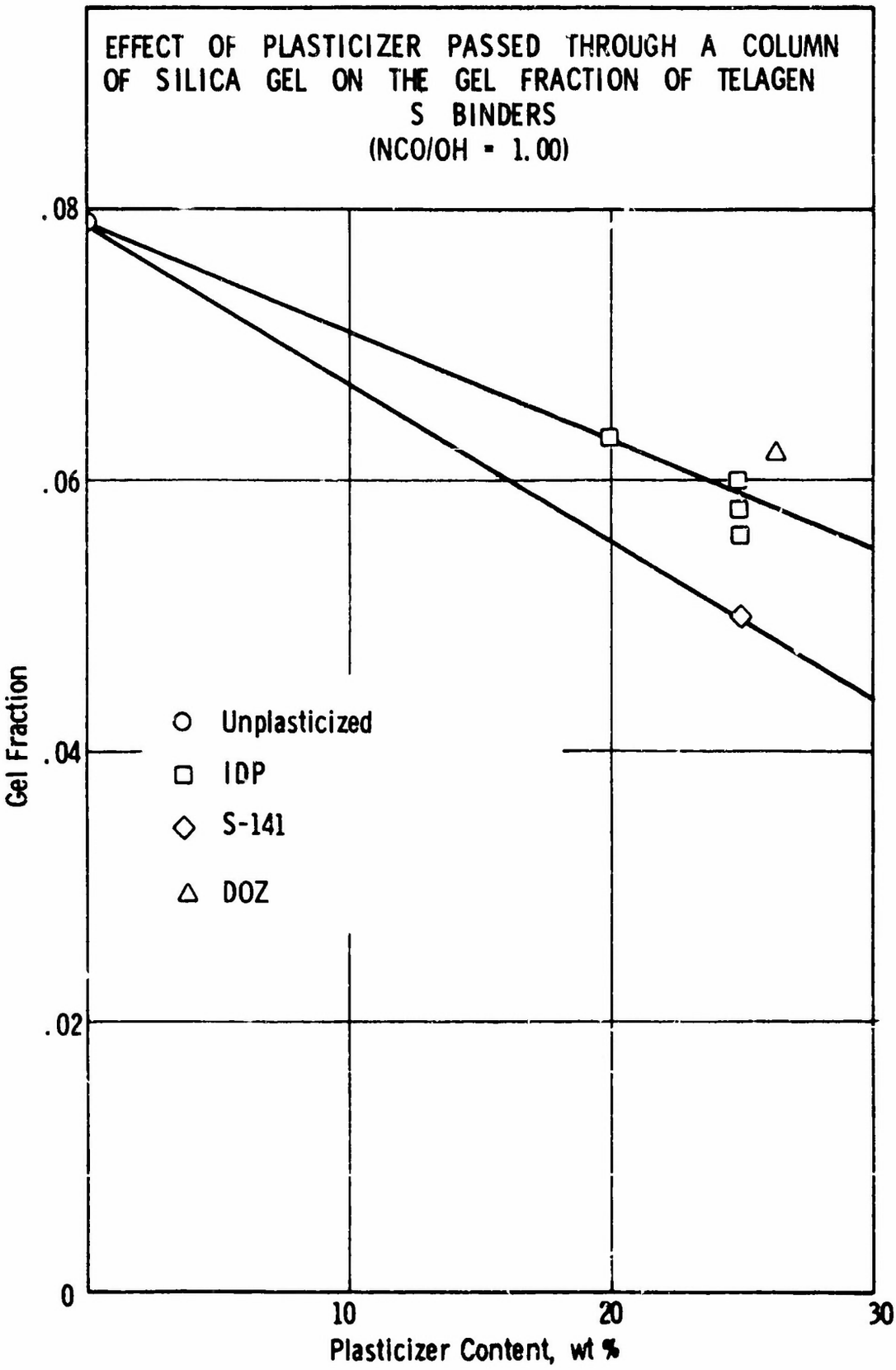
EFFECT OF PLASTICIZER PASSED THROUGH A COLUMN OF SILICA GEL ON THE GEL FRACTION OF TELAGEN S BINDERS
(NCO/OH = 1.00)
.08
.06
.04
.02
0
Gel Fraction
Unplasticized
IDP
S-141
DOZ
10
20
30
Plasticizer Content, wt %

Figure 13

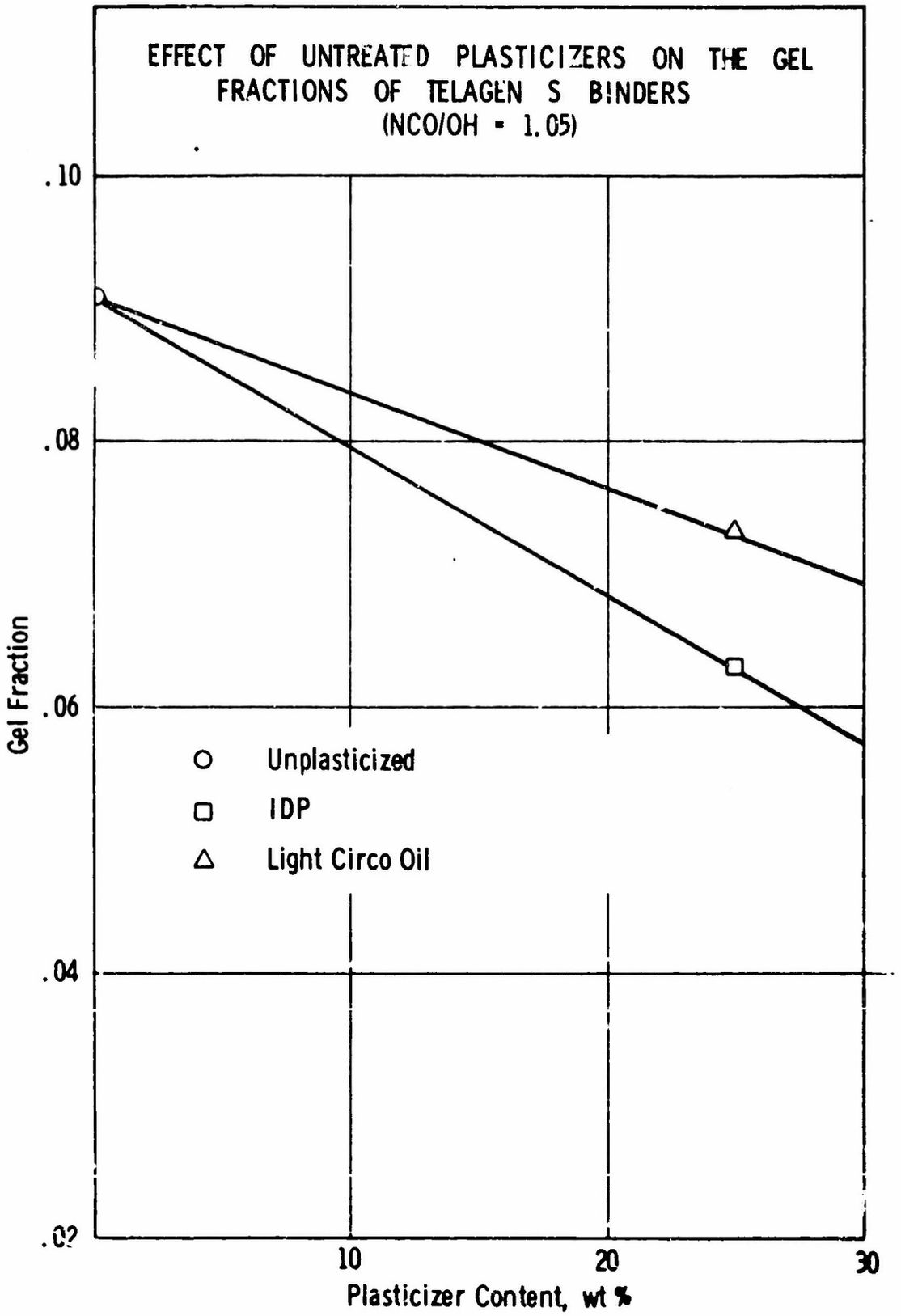
EFFECT OF UNTREATED PLASTICIZERS ON THE GEL FRACTIONS OF TELAGEN S BINDERS
(NCO/OH = 1.05)
.10
.08
.06
.04
.02
Gel Fraction
Unplasticized
IDP
Light Circo Oil
10
20
30
Plasticizer Content, wt %

Figure 14

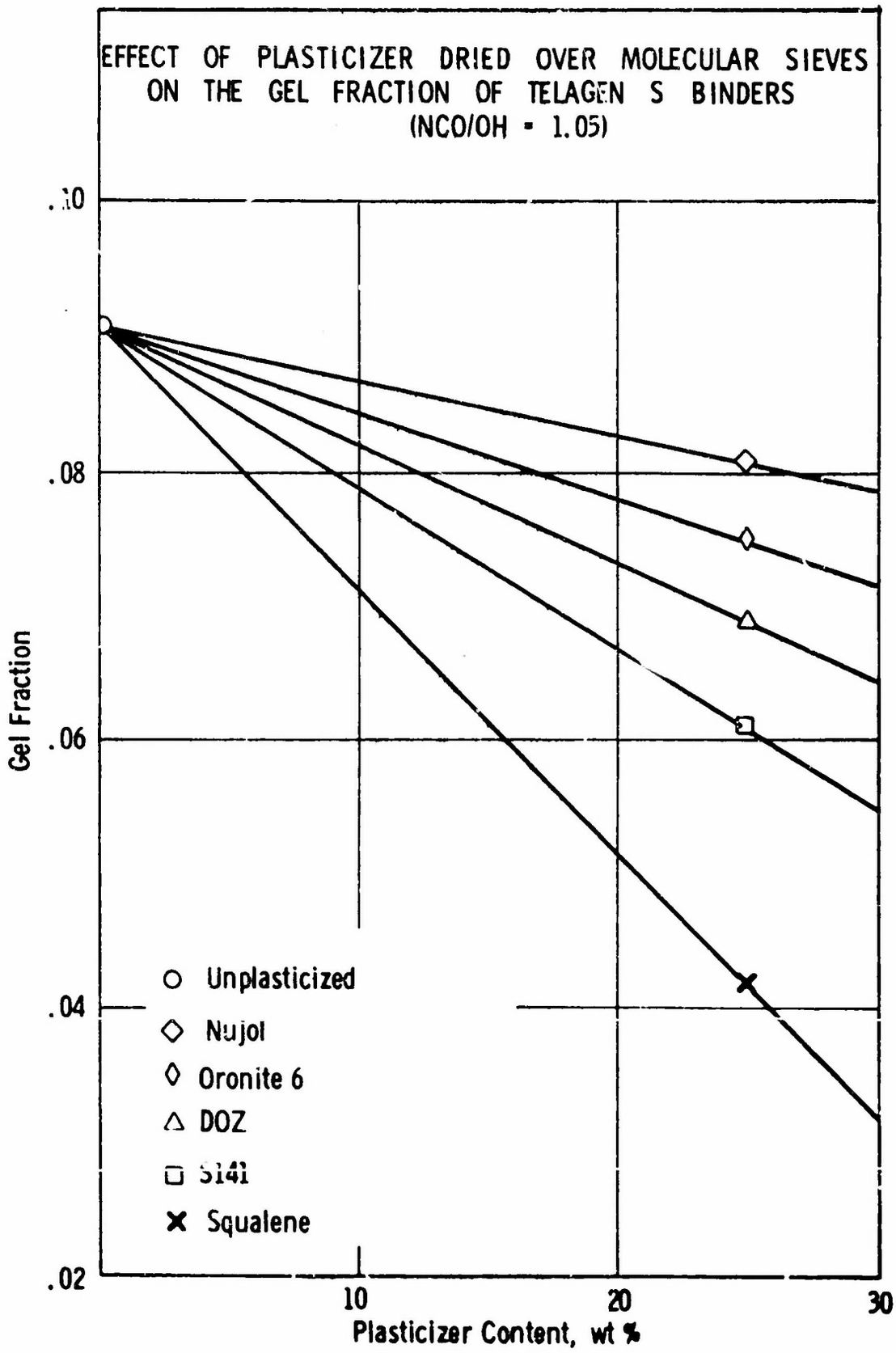
EFFECT OF PLASTICIZER DRIED OVER MOLECULAR SIEVES
ON THE GEL FRACTION OF TELAGEN S BINDERS
(NCO/OH = 1.05)
.10
.08
.06
.04
.02
Gel Fraction
10
20
30
Plasticizer Content, wt %
Unplasticized
Nujol
Oronite 6
DOZ
S141
Squalene

Figure 15

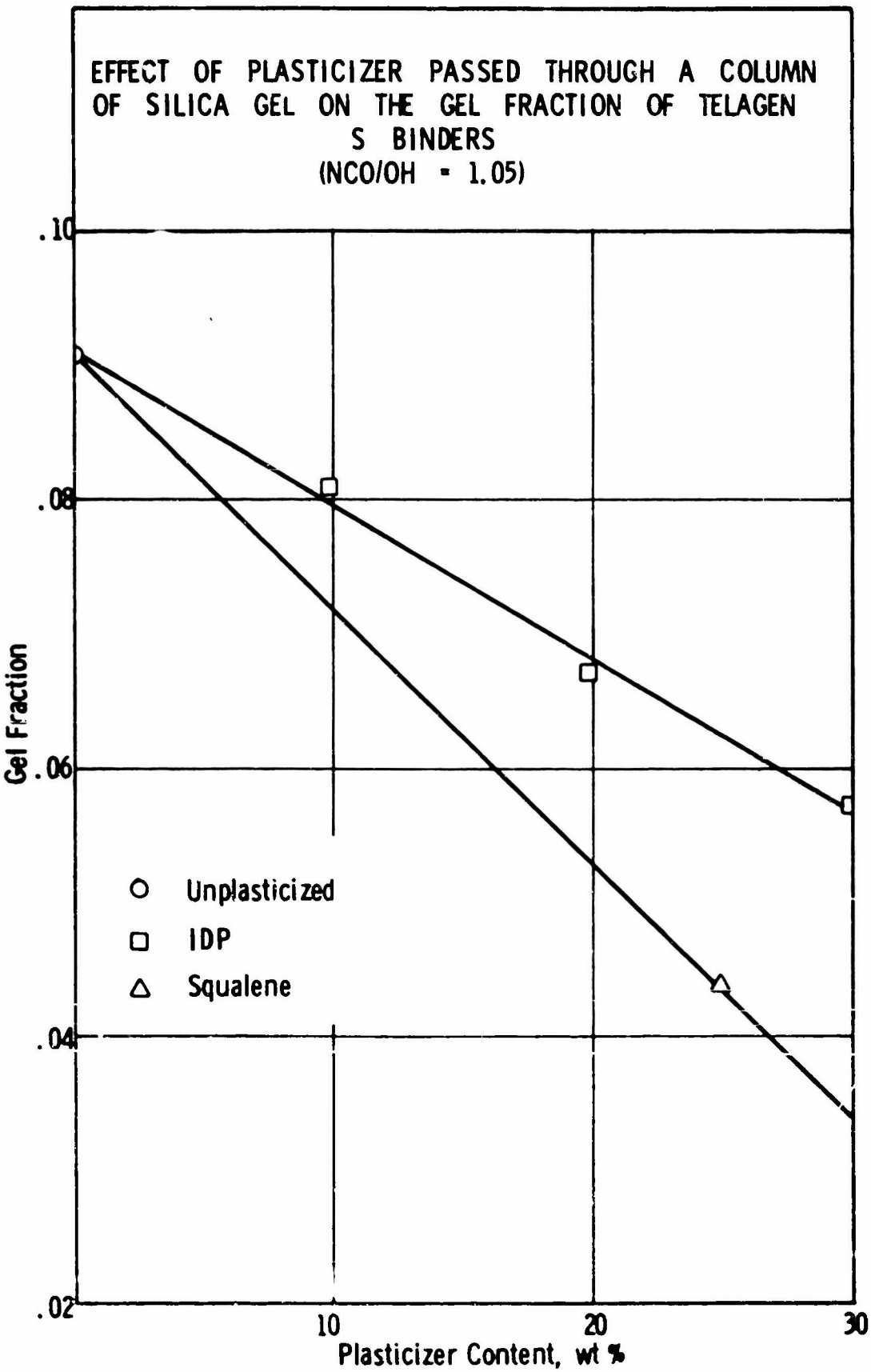
EFFECT OF PLASTICIZER PASSED THROUGH A COLUMN OF SILICA GEL ON THE GEL FRACTION OF TELAGEN S BINDERS
(NCO/OH = 1.05)
.10
.08
.06
.04
.02
Gel Fraction
Unplasticized
IDP
Squalene
10
20
30
Plasticizer Content, wt %

Figure 16

6) Conclusions

The study of plasticizers has indicated that many plasticizers seriously interfere with the cure reactions of the Telagen S-CTI-HDI binders. This effect may be quite general in solid propellant technology. Since the effect and the objective of plasticization is to reduce the modulus of a propellant, the modulus reduction caused by interference with cure reactions have not been noted. Further study is needed to better define the problem and to discover the true effect and value of solid propellant plasticizers.

c. Propellant Studies

Propellants were prepared to further test the effect of plasticizers. A study to check the optimum ratio of isocyanate to prepolymer was deferred until the effect of the plasticizers could be determined. The propellants were prepared and their properties are shown in Table 16.

The propellants were made in 50g batches and bars (3/8" x 3/8" x 2.7") were tested for uniaxial tensile behavior at 77°F. Only gross effects were observed by this procedure. The propellants were noticeably softer on the surface exposed to air. This phenomenon was also observed during work under Contract AF 04(611)-10386; but the surface softness is not detected with larger batches (>1-lb).

The castability at 135°F was determined by the Parallel Plate Plastimeter. This consists of two heavy glass plates on one of which is placed a cylindrical sample of propellant. The other glass plate is lowered on to the sample. The spread of the propellant is noted after 30 seconds. The change in castability with time is an indicator of the rate at which the propellant is curing. The propellants with the exception of no. 3 plasticised with S-141 had good to excellent initial castability.

Table 16

(U) EFFECT OF PLASTICIZERS ON THE MECHANICAL BEHAVIO

Reference No.	Plasticizer	Treatment[b]	NCO/OH	Castability at 135°F[c] Initial	1 hour	Cure days
1	Oronite-6	MS	1.05	20.5	19.5	
2	DOZ	MS	1.05	21	22	
3	S-141	MS	1.05	17	20	
4	Light Circo Oil	none	1.05	20	17[f]	
5	IDP	none	1.05	23	23	
6	Oronite-6	MS	1.05	21	21	
7	Nujol	MS	1.05	20	18[g]	
8	IDP	none	1.00	23	22	
9	IDP	SiO_2	1.00	-	-	
10	IDP	SiO_2	1.05	-	-	
11	IDP	SiO_2	1.10	-	-	
12[h]	IDP	SiO_2	1.00	-	-	

[a]All propellants were 50g batches and contained 75.6 vol % solids, Telagen S 90 eq.,

[b]MS = dried ober molecular sieves; SiO_2 = passed through column of SiO_2.

[c]Plastimeter reading (see final report Contract AF 04(611)-10386, p 166); >22 - exce

[d]15 sec.

[e]bond failure.

[f]2-1/2 hours.

[g]1.5 hours.

[h]DEA replaced by C-1.

Table 16

ON THE MECHANICAL BEHAVIOR OF TELAGEN S PROPELLANTS[a]

Stability at 135°F[c]		Cure Time,	Hardness,[d] Shore A			Mechanical Behavior at 77°F				
tial	1 hour	days at 135°F	Top	Side	Bottom	S_{nm} psi	S_{nb} psi	γ_{nm} %	γ_{nb} %	E_o psi
0.5	19.5	12	42	49	46	46	46	15	16	866[e]
1	22	12	43	67	72	129	129	18	18	1212[e]
7	20	12	14	48	48	58	58	23	25	354
0	17[f]	12	62	73	76	150	150	22	22	1740[e]
3	23	12	31	51	53	47	47	27	30	816
1	21	12	28	48	48	64	64	27	34	976
0	18[g]	7	43	70	72	110	110	20	20	1100
3	22	7	16	40	39	50	46	28	38	315
	-	8	63	70	70	137	137	25	25	1160
	-	8	53	65	73	141	141	28	28	1440
	-	8	71	80	80	186	186	24	24	2120
	-	8	30	35	35	61	54	32	43	420

solids, Telagen S 90 eq., DEA 1.0 eq and HDI:CTI = 4.0; plasticizer = 25 wt% of binder.
olumn of SiO_2.
-10386, p 166); ≥22 - excellent, 20-22 = good, 19-20 = fair, 16-19 = poor, and ≤16 = not castable.

Comparison of propellants with non-treated and treated IDP indicate the effect of plasticizer-curing agent interaction. The IDP passed through a column of SiO_2 gave propellants with better properties (compare 5 with 10 and 8 with 9).

These limited data also indicate that, for the propellants containing SiO_2 treated IDP, an NCO to OH ratio of 1.05 is best (compare propellants 9, 10 and 11).

During the propellant optimization studies made under Contract AF 04(611)-10386, it became apparent that binder reinforcement around the oxidizer was required. Diethanolamine was added to the propellant for this purpose. The theory was that the diethanolamine would be attracted to the oxidizer surface where it would react to form diethanolammonium perchlorate and ammonia. The amine salt could then react with isocyanate as a diol to reinforce the binder around the oxidizer. This theory assumed that the hydrogens on the nitrogen of protonated diethanolamine would not be available for reaction with the isocyanate.

In propellant No. 12 in Table 16, the diethanolamine was replaced by C-1, (N,N-di-(β-cyanoethyl)-2,3-dihydroxypropylamine) which has been used at Aerojet for some time to reinforce the oxidizer-binder interface. The result would indicate that diethanolamine is responsible for crosslinking in the propellant. Further studies are being made with C-1 to better evaluate it and to compare its effects with those of the diethanolamine.

d. Propellant Aging Studies

Propellants were aged at room temperature and at 180°F to study plasticizer loss. The study was designed to detect gross effects and was not a full scale program. The results are shown in Table 17.

The hardness data shows a great deal of scatter and a true trend is difficult to detect. Propellant No. 2 plasticized with DOZ appears to deteriorate, but this is the only case with a detectable trend. The tentative conclusion is that no degradation of the propellants occurred at the test conditions. A more detailed and extensive aging program is scheduled so this experiment was not pursued further.

6. Solvent Swelling

Under Contract AF 04(611)-10386 the swelling of binders and propellants was done exclusively with ethylene dichloride. There were many indications that this was not the best solvent for the isocyanate cured system which was developed. A further study of swelling solvents was initiated as part of the current contract.

A primary hydroxyl terminated Telagen S cured with a combination of CTI and HDI (theoretical crosslink density: 0.5×10^{-4} moles of crosslinker per gram of binder) was swollen in nitromethane, tetrahydrofuran, dioxane, chloroform, benzene, cyclohexane, n-hexane, methyl ethyl ketone, ethyl acetate, n-heptane, toluene, acetonitrile, and ethylene dichloride. Figure 17 shows the degree of swelling with time.

Although there are a few exceptions, most of the solvents achieved the maximum swelling in about seven days. Tetrahydrofuran reaches the maximum in about 3 days while dioxane was still increasing on the tenth day.

Table 17

(U) EFFECT OF STORAGE AT 77°F AND 180°F[a] ON THE HARDNESS[b] OF

Propellant[d] Reference No.	Storage Temp °F	Storage Time, we											
		0			1			2			3		
1	77	42	46	51	44	51	50	43	45	45	40	52	48
	180	42	46	51	50	50	49	44	54	53	55	66	66
	200												
2	77	48	77	79	48	73	76	52	74	77	53	71	71
	180	48	77	79	48	76	79	44	72	75	50	62	62
	200												
3	77	15	46	46	12	49	47	16	46	49	15	48	42
	180	15	46	46	15	47	46	19	53	51	20	36	45
	200												
4	77	72	76	76	60	74	74	63	73	76	63	74	78
	180	72	76	76	65	73	71	71	83	76	68	84	83
	200												
5	77	28	62	62	26	51	56	28	57	56	30	54	58
	180	28	62	62	28	61	75	43	78	70	58	79	77
	200												
6	77	23	44	44	20	43	46	23	48	47	27	47	50
	180	23	44	44	23	42	45	36	58	58	34	49	53
	200												
9	180	63	70	70	-	-	-	73	63	60	-	-	-
10	180	53	65	73	-	-	-	62	74	70	-	-	-
11	180	71	80	80	-	-	-	80	77	80	-	-	-
12	180	30	35	35	-	-	-	-	-	-	-	-	-

[a]Stored at 180°F for 4 weeks, then at 200°F.

[b]Table entries are hardnesses at top, side, and bottom of sample.

[c]Composition given in fac

[d]Further data see Table 1

Table 17

:7°F AND 180°F[a] ON THE HARDNESS[b] OF WORKHORSE PROPELLANTS[c]

Storage Time, weeks															
2			3			4			5			7			
43	45	45	40	52	48	-	-	-	43	53	50	-	-	-	
44	58	53	55	66	66	-	-	-	-	-	-	-	-	-	
									61	63	55	63	55	58	
52	74	77	53	71	71	-	-	-	42	45	80	-	-	-	
44	72	75	50	62	62	-	-	-	-	-	-	-	-	-	
									34	54	52	-	54	52	
16	46	49	15	48	42	-	-	-	15	47	46	-	-	-	
19	53	51	20	36	45	-	-	-	-	-	-	-	-	-	
									18	32	32	-	40	41	
63	73	76	63	74	78	-	-	-	56	74	74	-	-	-	
71	83	76	68	84	83	-	-	-	-	-	-	-	-	-	
									70	84	80	61	70	68	
28	57	56	30	54	58	-	-	-	28	55	57	-	-	-	
43	78	70	58	79	77	-	-	-	-	-	-	-	-	-	
									61	66	64	59	86	76	
23	48	47	27	47	50	-	-	-	18	50	46	-	-	-	
36	58	58	34	49	53	-	-	-	-	-	-	-	-	-	
									24	44	39	50	50	51	
73	63	60	-	-	-	72	84	78	-	-	-	-	-	-	
62	74	70	-	-	-	84	88	78	-	-	-	-	-	-	
80	77	80	-	-	-	89	84	86	-	-	-	-	-	-	
-	-	-	-	-	-	66	66	60	-	-	-	-	-	-	

[c]Composition given in footnote a, Table 16.

sample. [d]Further data see Table 16 .

2

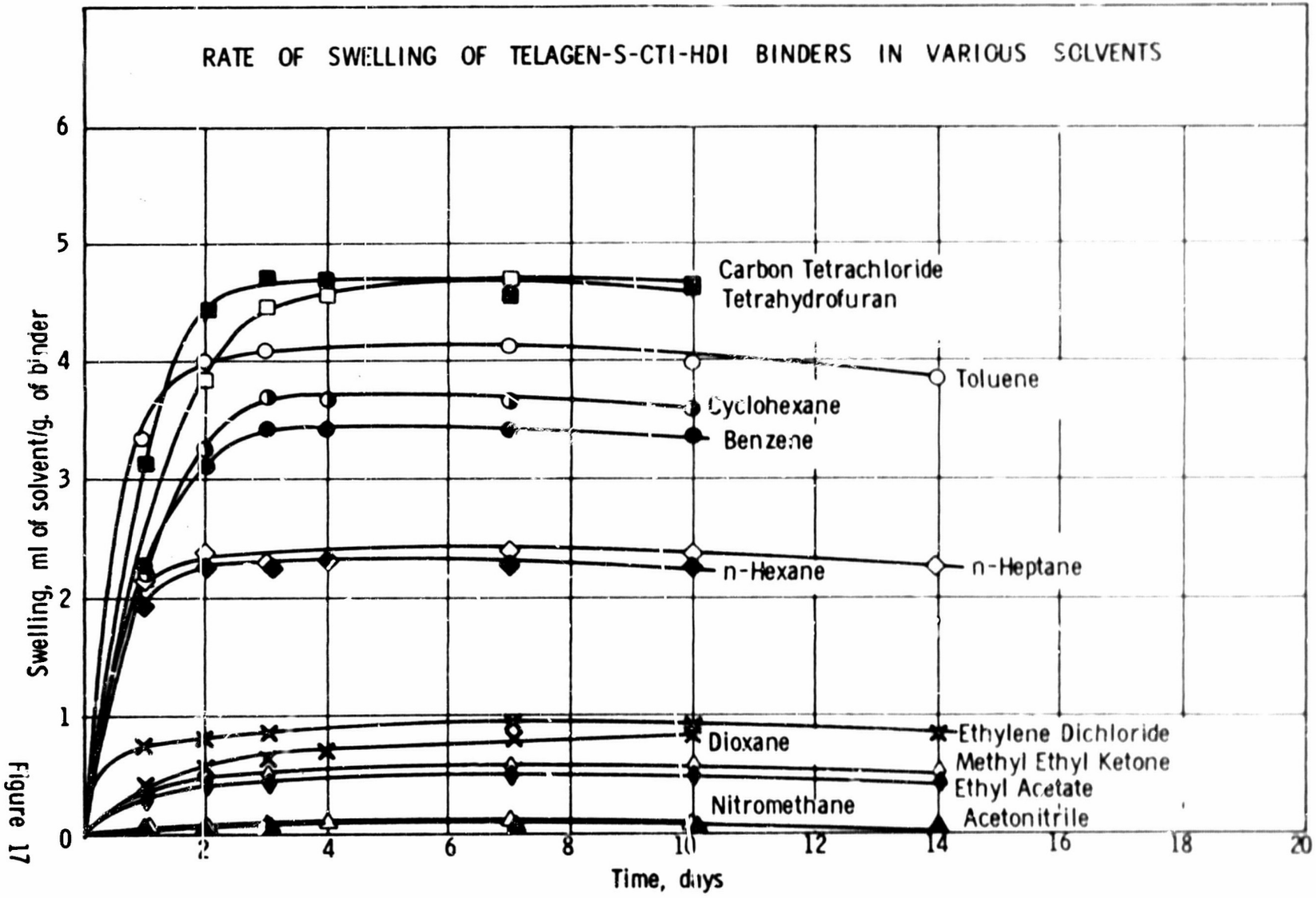
RATE OF SWELLING OF TELAGEN-S-CTI-HDI BINDERS IN VARIOUS SOLVENTS
Swelling, ml of solvent/g. of binder
Time, days
0
1
2
3
4
5
6
2
4
6
8
10
12
14
16
18
20
Carbon Tetrachloride
Tetrahydrofuran
Toluene
Cyclohexane
Benzene
n-Hexane
n-Heptane
Dioxane
Ethylene Dichloride
Methyl Ethyl Ketone
Ethyl Acetate
Nitromethane
Acetonitrile

Figure 17

After reaching the maximum, the swelling decreased slowly. The solvents continued to extract soluble material, but this extractable material did not account for the decrease in swelling.

Figure 18 indicates the relation between the maximum swelling for each solvent and the cohesive energy density (CED) of the solvent. The solvents and their cohesive energy densities are given in Table 18.

7. Mooney-Rivlin Constants

Mooney-Rivlin plots of all binder mechanical properties data were made and the values of the C_1 and C_2 constants were derived. These are shown in Table 9.

Data obtained under Contract AF 04(611)-10386 indicated a linear correspondence of the C_1 constant for carboxy-terminated Telagen S cured with epoxides or with aziridines and the crosslink densities of these polymers. The C_1 constant for Telagen S-CTI-HDI elastomers showed no such correlation (see Figure 49 of Final Report, AFRPL-TR-66-40, Contract AF 04(611)-10386).

Data accumulated under the present program show that the C_1 constants of plasticized Telagen S-CTI-HDI binders do correlate linearly with the gel fraction of toluene-swollen samples (Figure 8). For this reason a correlation with crosslink density may be possible and will be sought when the data are available.

The meaning of the C_2 constant with respect to the polymer properties is not known. Figure 20 indicates that C_2 is not a completely independent parameter, but depends upon C_1. The line represents the loci of points representing a one for one relation.

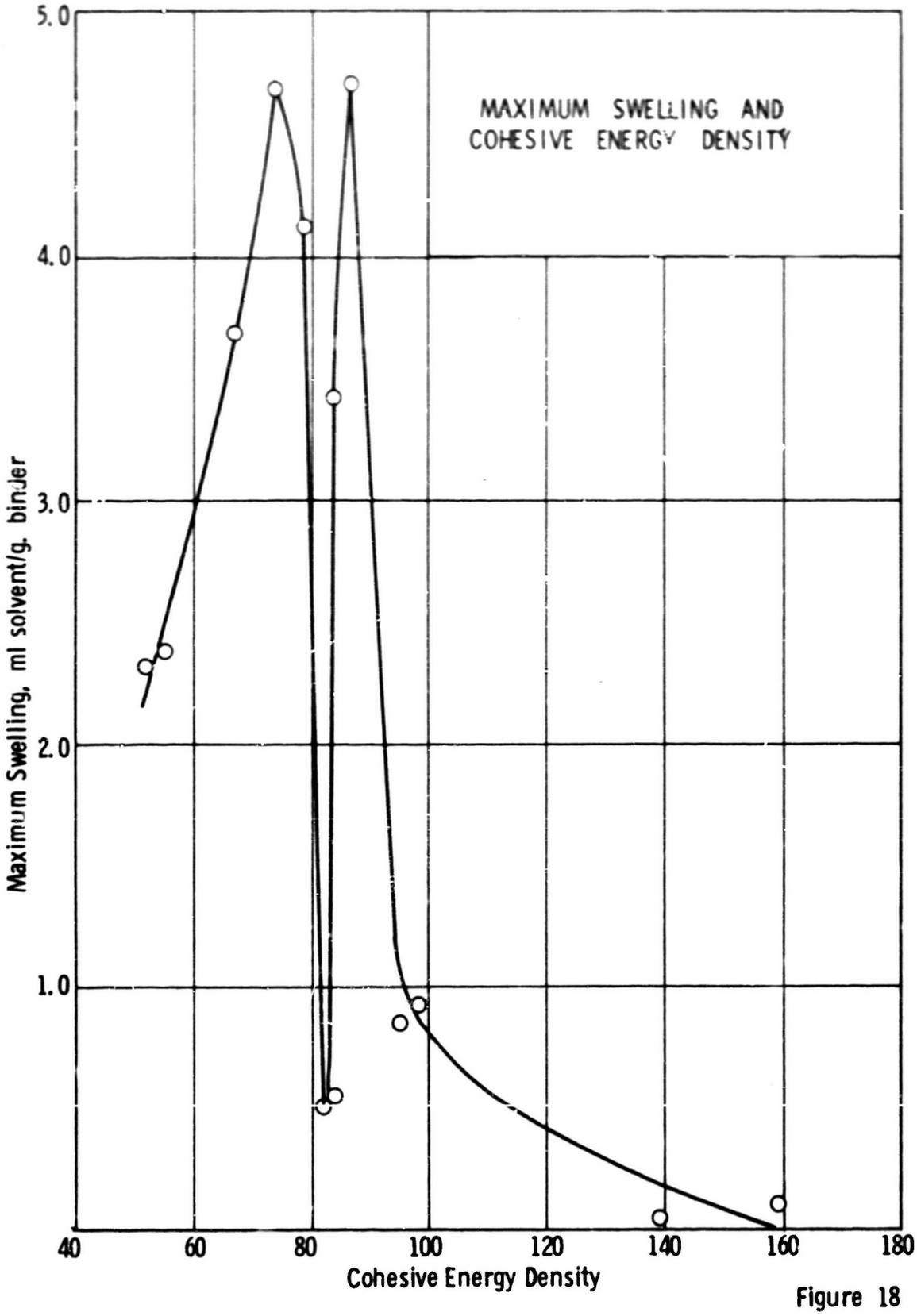
MAXIMUM SWELLING AND
COHESIVE ENERGY DENSITY
Maximum Swelling, ml solvent/g. binder
5.0
4.0
3.0
2.0
1.0
40
60
80
100
120
140
160
180
Cohesive Energy Density

Figure 18

Table 18

(U) MAXIMUM SWELLING AND THE COHESIVE ENERGY DENSITIES OF SOLVENTS

Solvent	CED	Maximum Swelling ml solvent/g binder
Nitromethane	159	0.11
Acetonitrile	139	0.05
Ethylene Dichloride	98.1	0.92
Dioxane	94.6	0.85
Tetrahydrofuran	86.8	4.70
Benzene	83.6	3.42
Methyl Ethyl Ketone	81.7	0.55
Ethyl Acetate	81.6	0.50
Toluene	79.3	4.12
Carbon Tetrachloride	73.6	4.68
Cyclohexane	66.8	3.68
n-Heptane	55.0	2.38
n-Hexane	52.4	2.32

The maximum swelling - CED curve shows two separate peaks, at CED of 73.6 and 86.8. The meaning of this phenomenon is not known. The best solvents for swelling the Telagen S-HDI-CTI binder are carbon tetrachloride and tetrahydrofuran.

The swelling data presented in Figures 17 and 18 and in Table 18 have not been corrected for solubles, but the solubles were minor (<10%).

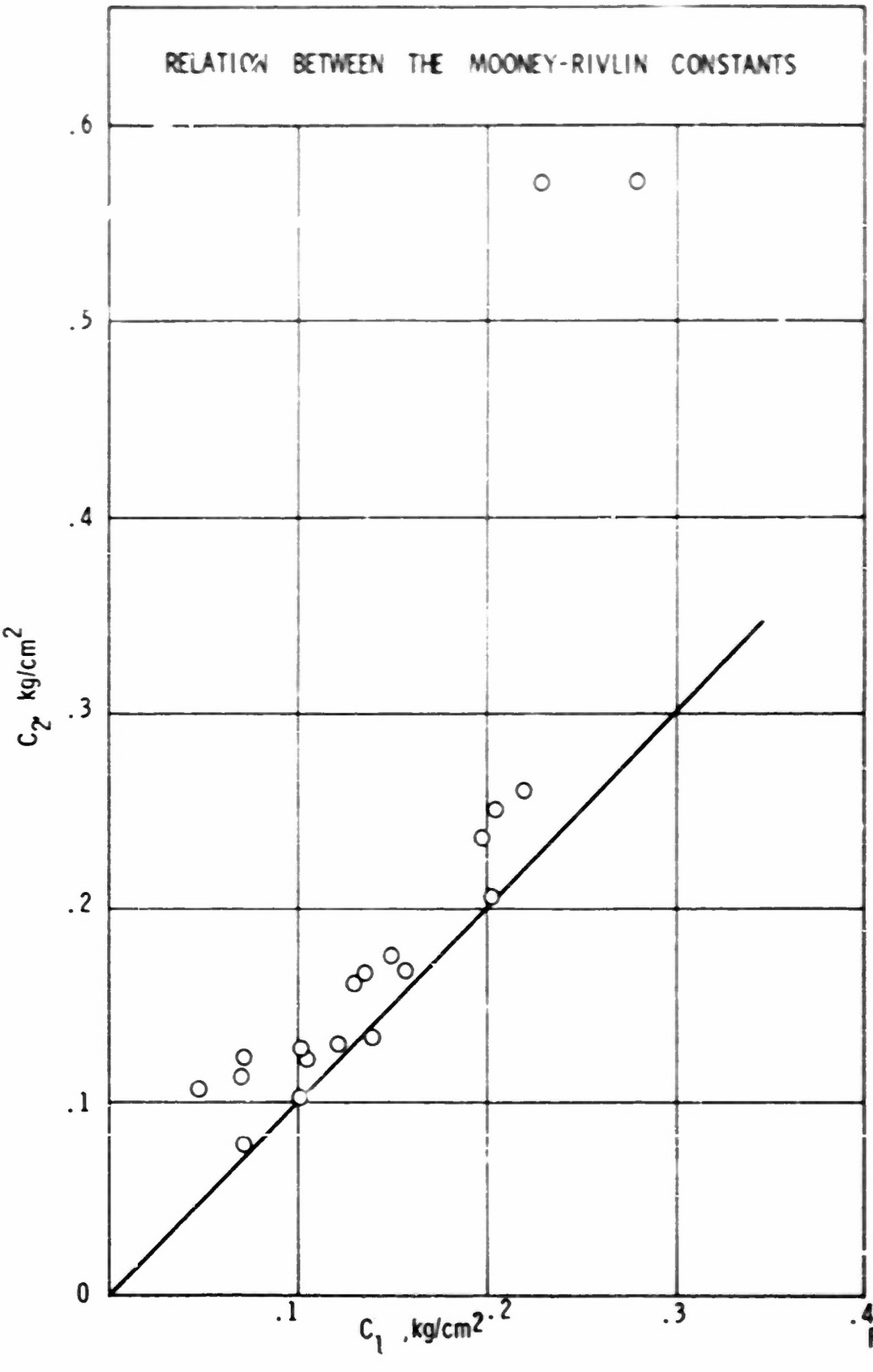
RELATION BETWEEN THE MOONEY-RIVLIN CONSTANTS
.6
.5
.4
.3
.2
.1
0
C_2, kg/cm^2
.1
.2
.3
.4
C_1, kg/cm^2

Figure 20

8. Differential Thermal Behavior and Crosslink Densities of Telagen S Binders

The decomposition of isocyanate-cured Telagen S binders of various crosslink densities was studied by differential thermal analysis. A linear relationship of the crosslink density with the decomposition temperature was discovered (Figure 21).

9. Maximum Solids Loaded Propellant

a. Solids Loading and Packing

1) Ratio of Solids to Binder Volumes

One of the advantages of a propellant binder with a highly efficient network structure is its ability to retain good mechanical properties when loaded with a greater amount of ballistic solids. Notwithstanding this advantage the problem of achieving a higher solids loading without loss of mechanical properties is a difficult one. This is demonstrated by the ratio of the solids volume to the binder volume (including the plasticizer) and the volume fraction of solids for a number of actual and projected systems with a saturated hydrocarbon binder (Table 19).

As the solids loading increases beyond the state-of-art value of 88 wt%, the ratio of the solids volume to binder volume increases greatly. This ratio becomes even greater at low temperature since the volume of the binder decreases more rapidly than that of the filler.

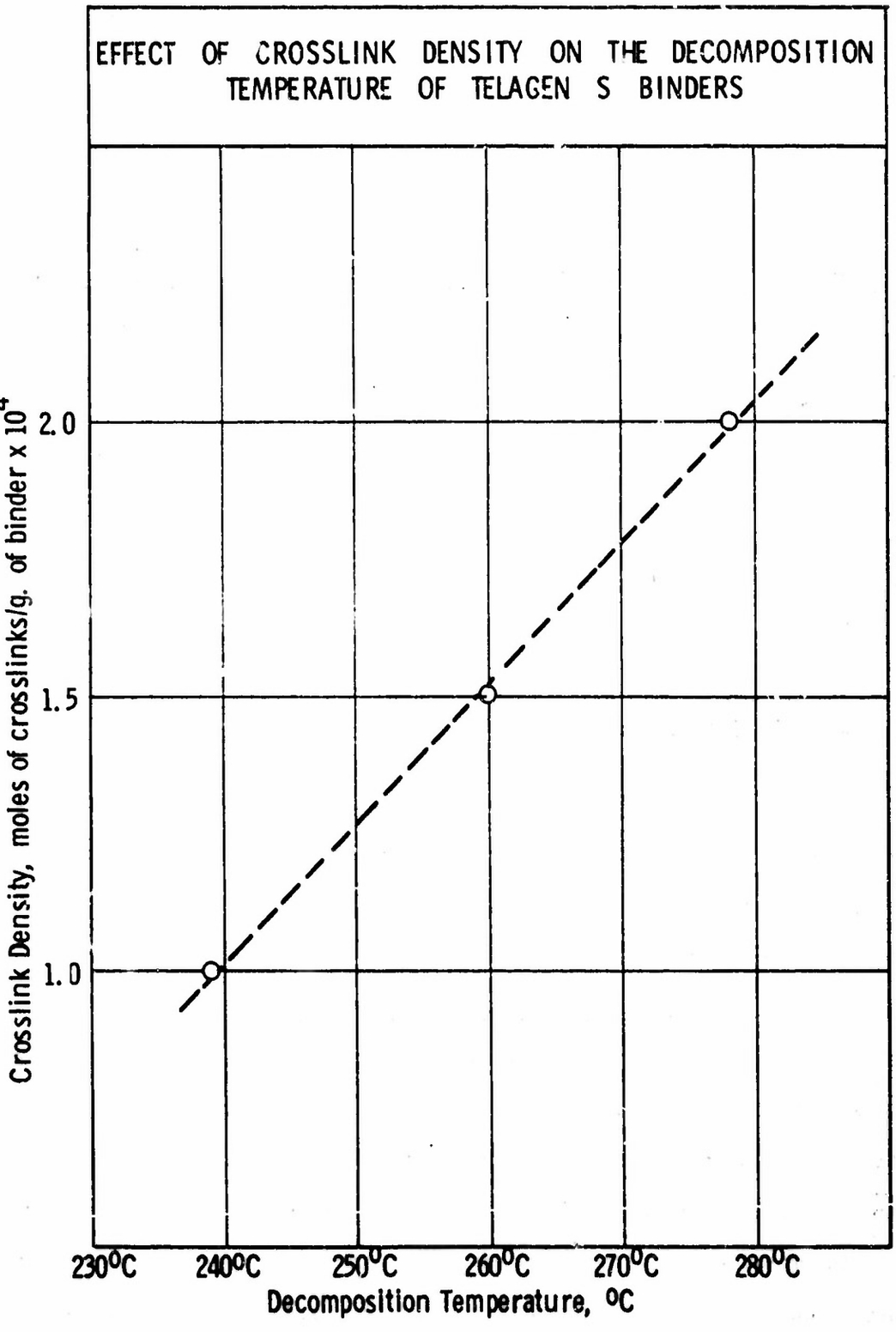
EFFECT OF CROSSLINK DENSITY ON THE DECOMPOSITION TEMPERATURE OF TELAGEN S BINDERS
Crosslink Density, moles of crosslinks/g. of binder x 10^4
2.0
1.5
1.0
230°C
240°C
250°C
260°C
270°C
280°C
Decomposition Temperature, °C

Figure 21

Table 19

(U) THE RATIO OF SOLIDS TO BINDER VOLUMES AND VOLUME FRACTION OF SOLIDS FOR VARIOUS PROPELLANT SYSTEMS

Propellant	Wt% Solids	Volume Fraction of Solids	Volume of Solids / Volume of Binder
Polaris	75	62.4	1.6
Minuteman Wing II (2nd Stage)	82.2	69.0	2.2
Tartar (sustainer)	82	70.0	2.3
Minuteman Wing VI (2nd Stage)	88	76.6	3.3
System 1[a]	90	80.2	4.1
System 2[a]	92	84.0	5.2

[a]System 1: 80% NH_4ClO_4, 10% Al; System 2: 84% NH_4ClO_4, 8% Al.

As the solids loading increases beyond the state-of-art value of 88 wt%, the ratio of the solids volume to binder volume increases greatly. This ratio becomes even greater at low temperature since the volume of the binder decreases more rapidly than that of the filler.

2) Importance of Particle Packing

The importance of packing of solid particles is well known as exemplified by the extensive use of bi- and trimodal particle blends in solid propellants to obtain improved mechanical behavior. The ballistic requirements will normally establish an average particle size for the fillers of a solid propellant but there are limitless numbers of particle size distributions which will have the same average particle size. As a result the task

of determining which blend of particle size distributions will achieve the highest solids loading in a propellant with reasonable mechanical properties is a tedious one.

b. Effect of Packing on Viscosity of Filled Liquids

A convenient method for determining the effectiveness of particle packing is by measuring the effect of particle packing on the viscosity of a liquid. The Eilers equation[1] shown below relates the relative viscosity (η_r) of a suspension to particle packing and loading.

$$\eta_r = \frac{\eta}{\eta_o} = \left[1 + \frac{1.25\,\phi}{1-(\phi/\phi_f)}\right]^2$$

where η and η_o are the viscosities of the filled and unfilled liquids, ϕ is the volume fraction of solids, and ϕ_f is the maximum volume fraction solids (at which $\eta_r = \infty$). The parameter ϕ_f is a function of the particle packing, and for uniform sized spheres is 0.74 by theory.

Measurements of the viscosities of monodispersed suspensions fit an equation of the form proposed by Eilers with $\phi_f = 0.605$ which is approximately the theoretical for orthorhombic packing.

---

(1) H. Eilers, Kolloid. Zeit. 102, 154 (1954)

c. Similarity of Viscosity and Modulus of Filled Systems

The use of Eilers relation with the viscosity (η) replaced by Young's modulus (E)[1] has been proposed for the analogous elastic problem of rubbers containing fillers. Some success was achieved by T. Smith[2] in application of an equation of the Eilers type to solid propellants.

Therefore, the best packing of particles of different sizes will give a slurry with the lowest viscosity and for a given solids content will give a propellant with the lowest modulus. The maximum loading that such a packing would allow must, of course, be determined by its effect in a propellant system.

a Effect of Particle Size Distribution on Viscosity

The use of particles of different size allows much more efficient packing of particles. Horsfield[3] calculated that a suspension with a solids concentration of 85.1% by volume is possible by use of particles of five different sizes.

A number of investigators have experimentally studied suspension of bimodal distributions of solids up to 74% by volume. These studies show that the viscosity of concentrated suspensions could decrease markedly if the particle size ratio and relative amounts of small to large spheres were chosen properly.

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(1) J. Rehner, J. Appl. Phys., 14, 638 (1943).
(2) T. L. Smith, Trans. Soc. of Rheology, 3, 113 (1959).
(3) H. Horsfield, J. Soc. Chem. Ind., 5, 107 1934).

e. Approach

The approach to more highly loaded solid propellants consists of two distinct steps. The first involves the determination of the blends of available oxidizer particle sizes which give a slurry with a minimum viscoeity (best packing of particles). The second step is the determination of the maximum solids loading which may be achieved with the blend determined in the first step. The work reported here is the first step of this approach.

f. Particle Sizes

Some available particle sizes of NH_4ClO_4, with the exception of 3-9μ particlee which were used as received, were screened to a narrower range of particle sizes for a study of the effect of particle size on the relative viscoeity of a slurry.

Screens were stacked as indicated in Table 20, and vibrated for approximately a half hour. The oxidizer remaining on each of the screens was weighed and the sizes to be used were separated. The oxidizers used were 3-9μ , 43-104μ , 104-250μ , and 250-495μ . These will be referred to as monomodal systeme.

g. Viscosity Measurements

The viscosity measurements were made with a Haake Rotovisko (Type RV) viscometer equipped with a multiple measuring head (50-500) and the Haake Circulator (Type RBD) at 30°C. Varioue volume fractions of each of the monomodal systems were made up in Cronite-6, using a density of 1.95 g/cc for the NH_4ClO_4 and 0.84 g/cc for the Cronite-6.

Table 20

(U) SCREENING OF NH_4ClO_4 INTO NARROW PARTICLE SIZE DISTRIBUTIONS

Tyler Sieve No.	Sieve Opening Size μ	NH_4ClO_4 Initial Particle Blend				
		+48 % of Total[a]	+48 % of Total[a]	Unground % of Total[a]	Slow-Speed % of Total[a]	Slow-Speed % of Total[a]
10	1650	0.0	0.0	-[b]	-[b]	-[b]
16	991	0.033	0.0	-	-	-
20[c]	833[c]	.027	0.0	-	-	-
32	495	7.52	15.60	-	-	-
48[c]	297[c]	89.80	80.90	15.0	-	0.67
60	250	3.19	2.68	15.7	6.64	4.83
100[c]	149[c]	-[b]	-[b]	43.2	49.4	40.8
150	104	-	-	17.5	20.1	22.30
200[c]	74[c]	-	-	4.72	11.2	12.05
325	43	-	-	1.85	8.4	11.55

[a] % retained on screen.

[b] Dashes indicate screens not used.

[c] Parantheses indicate particle sizes combined.

One hundred milliliters of the lowest solids loading indicated on each size were made up, the viscosity measured, the solids loading was increased by addition of NH_4ClO_4 to the original and the measurement repeated. The upper limit of the solids loading was determined by lack of flow characteristics or lumpiness. Viscosity measurements in this area were very inaccurate and are not reported. The lower limits of the solids loading were characterized by rapid settling of the solids, particularly the larger particles. Reasonably accurate viscosities for the slurries which tended to settle rapidly were obtained by plotting the viscosity vs time and extrapolating to zero time.

h. Results

The results of the viscosity measurements are given in Table 21, with the exception of the 20-32 mesh size which were very inaccurate. Viscosities were initially obtained by measuring each sample at the highest attainable shear rate. The data obtained in this manner were inconsistent since the viscosities varied widely with shear rate. All data reported here were obtained at a spindle rate of 162 RPM (speed factor 3) since measurements at this rate could be obtained for all the samples involved.

A plot of relative viscosity vs volume fraction of solids shown in Figure 22 indicates the increase of relative viscosity with decreasing particle size. The viscosity of Oronite-6 (η) is 39.4 centipoise at 30°C and is Newtonian.

The data adhere well to the Eilers equations,

$$\eta_r = \left[1 + \frac{A\phi}{1-B\phi}\right]^2 \qquad \text{A and B constant}$$

which can be put in the form

$$\frac{1}{\eta_r^{1/2}-1} = \frac{1}{A}\left(\frac{1}{\phi} - B\right)$$

Table 21

(U) EFFECT OF PARTICLE SIZE AND SOLIDS LOADING OF THE VISCOSITY OF NH_4ClO_4 - ORONITE-6 SLURRIES

Particle Size μ	Volume Fraction Solids (ϕ)	Viscosity (η) (Centipoise)	Relative Viscosity (η_r)	$\eta_r^{1/2}-1$
3-9	0.10	66.18	1.68	0.29
	0.20	164.35	4.17	1.04
	0.25	487.54	12.37	2.52
	0.275	414.74	10.53	2.24
	0.30	825.07	20.94	3.57
	0.325	904.48	22.96	3.78
43-104	0.20	88.24	2.24	0.49
	0.30	175.38	4.45	1.11
	0.35	364.00	9.24	2.04
	0.40	617.70	15.68	2.96
	0.425	1103.03	28.00	4.29
	0.45	1531.01	38.86	5.24
104-250	0.20	80.08	2.03	0.42
		101.38	2.57	0.60
	0.25	112.95	2.87	0.70
	0.30	159.72	4.05	1.08
		185.00	4.70	1.17
	0.35	147.82	3.75	0.94
		273.14	6.94	1.63
	.40	262.52	6.66	1.58
	0.45	500.78	12.71	2.56
	0.55	2528.38	64.17	7.04
250-495	0.25	78.09	1.98	0.41
	0.35	153.32	3.89	0.97
	0.45	420.70	10.68	2.27
	0.50	904.48	22.96	3.79
	0.55	1882.36	47.78	5.81

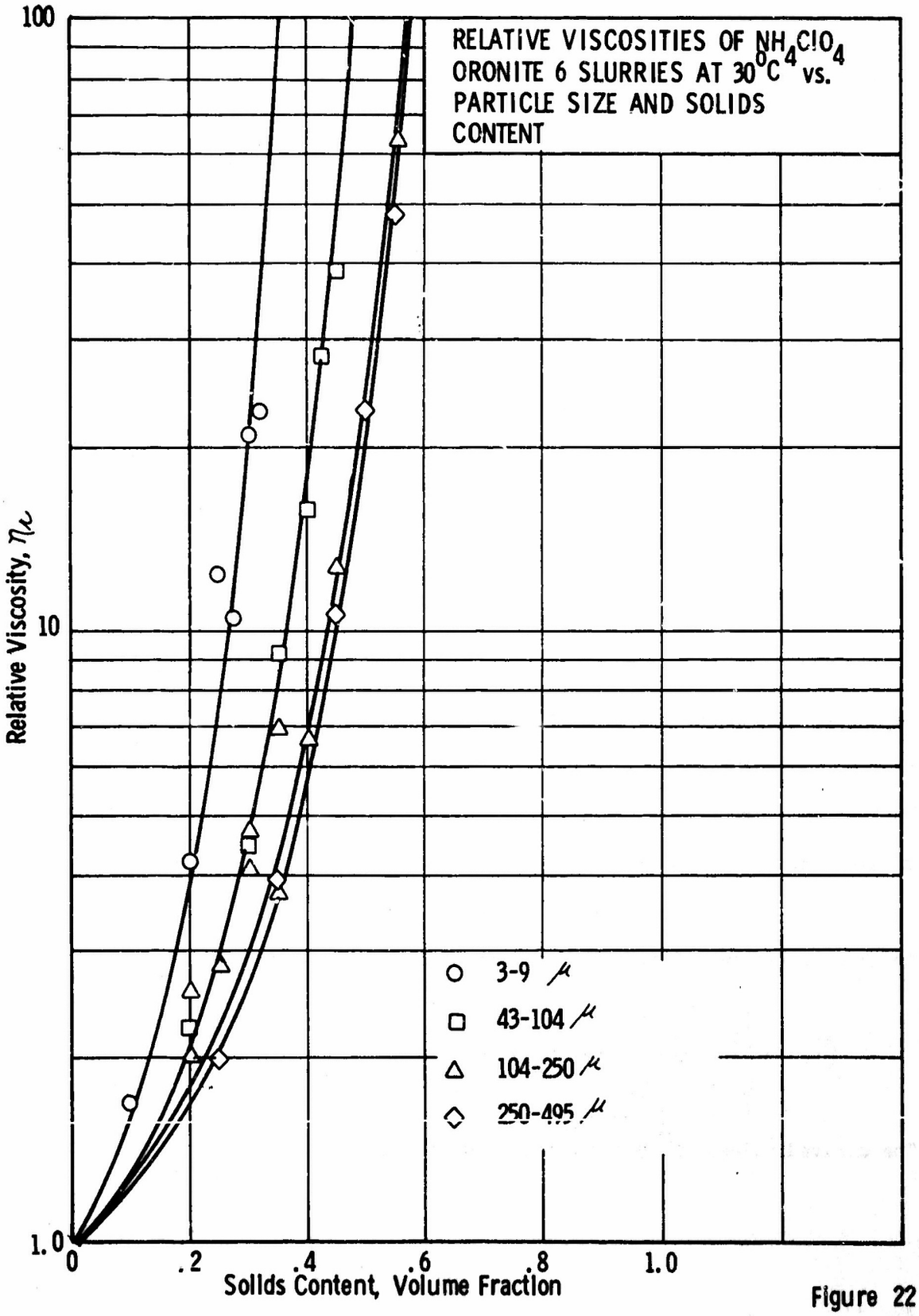

RELATIVE VISCOSITIES OF NH_4ClO_4 ORONITE 6 SLURRIES AT 30°C vs. PARTICLE SIZE AND SOLIDS CONTENT
Relative Viscosity, η_r
100
10
1.0
0
.2
.4
.6
.8
1.0
Solids Content, Volume Fraction
3-9 μ
43-104 μ
104-250 μ
250-495 μ

Figure 22

Figure 23 shows a plot of $\frac{1}{\eta_r^{1/2}-1}$ vs $\frac{1}{\phi}$. The straight lines indicate adherence to the above equation. Table 22 indicates the values derived for A and B.

Table 22

(U) VARIATION OF CONSTANTS A AND B WITH PARTICLE SIZE

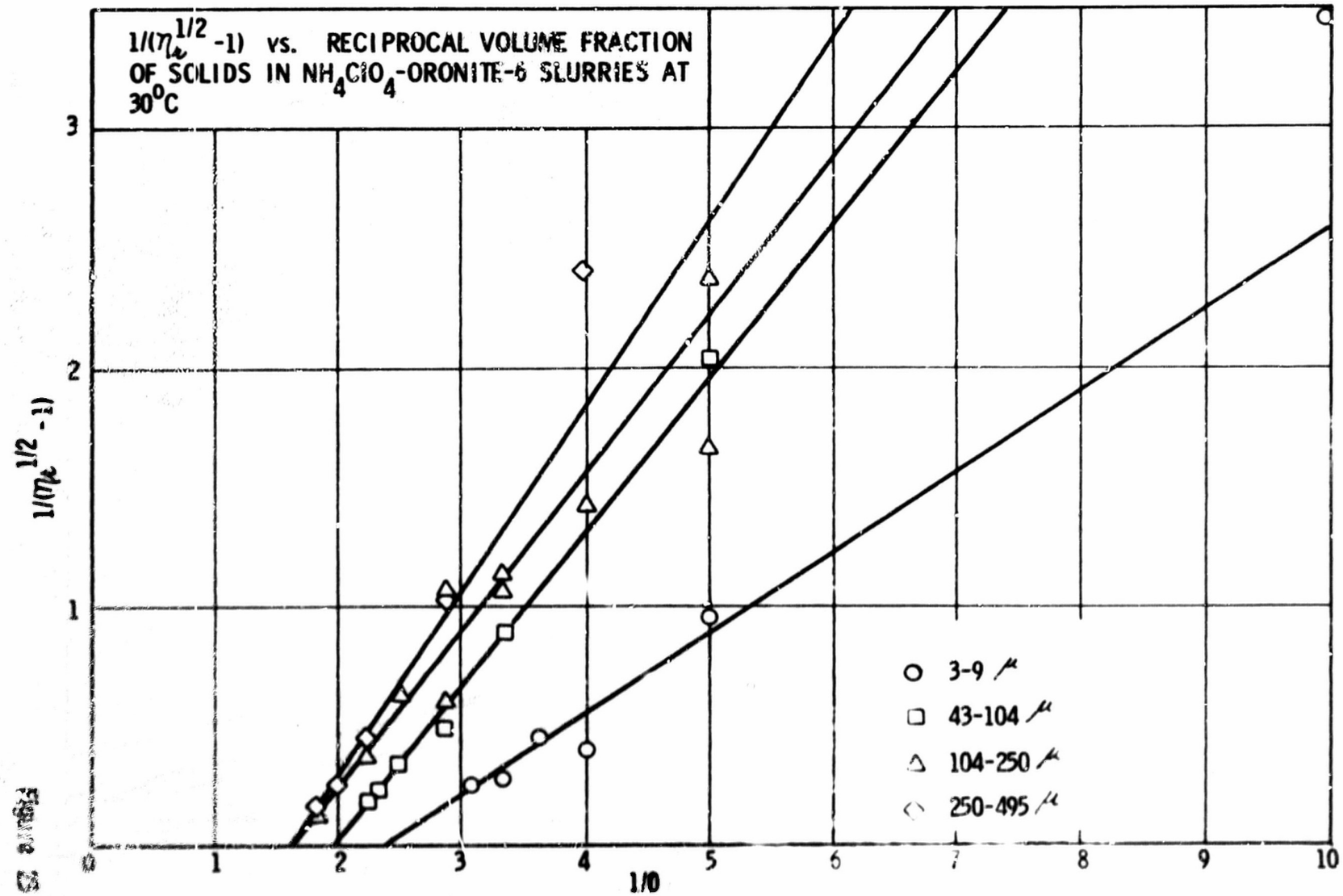
Particle Size, μ	Solids Content, Vol. Fraction	A	B	1/B
3-9	0.1 - 0.325	2.88	2.32	0.43
43-104	0.2 - 0.45	1.55	1.96	0.51
104-250	0.2 - 0.55	1.57	1.63	0.61
250-495	0.25 - 0.55	1.59	1.59	0.63

The physical significance of A is not known but it may depend either on the particle size or the particle size distribution. The data seem to favor the dependence of A on the latter rather than on the former. Further experiments may clarify this point. The constant, 1/B, represents the volume fraction of solids at which the relative viscosity becomes infinite.

The data of Table 21 could also be plotted as in Figure 24 to give linear relations. These lines indicate the relation

$$\eta_r = \left\{1 + \exp\left[\frac{1}{2.303}\left(C\phi + D\right)\right]\right\}^2$$

The derived values for C and D are shown in Table 23.


$1/(\eta_r^{1/2}-1)$ vs. RECIPROCAL VOLUME FRACTION OF SOLIDS IN NH_4ClO_4-ORONITE-6 SLURRIES AT 30°C
$1/(\eta_r^{1/2}-1)$
1/0
0
1
2
3
4
5
6
7
8
9
10
3-9 μ
43-104 μ
104-250 μ
250-495 μ

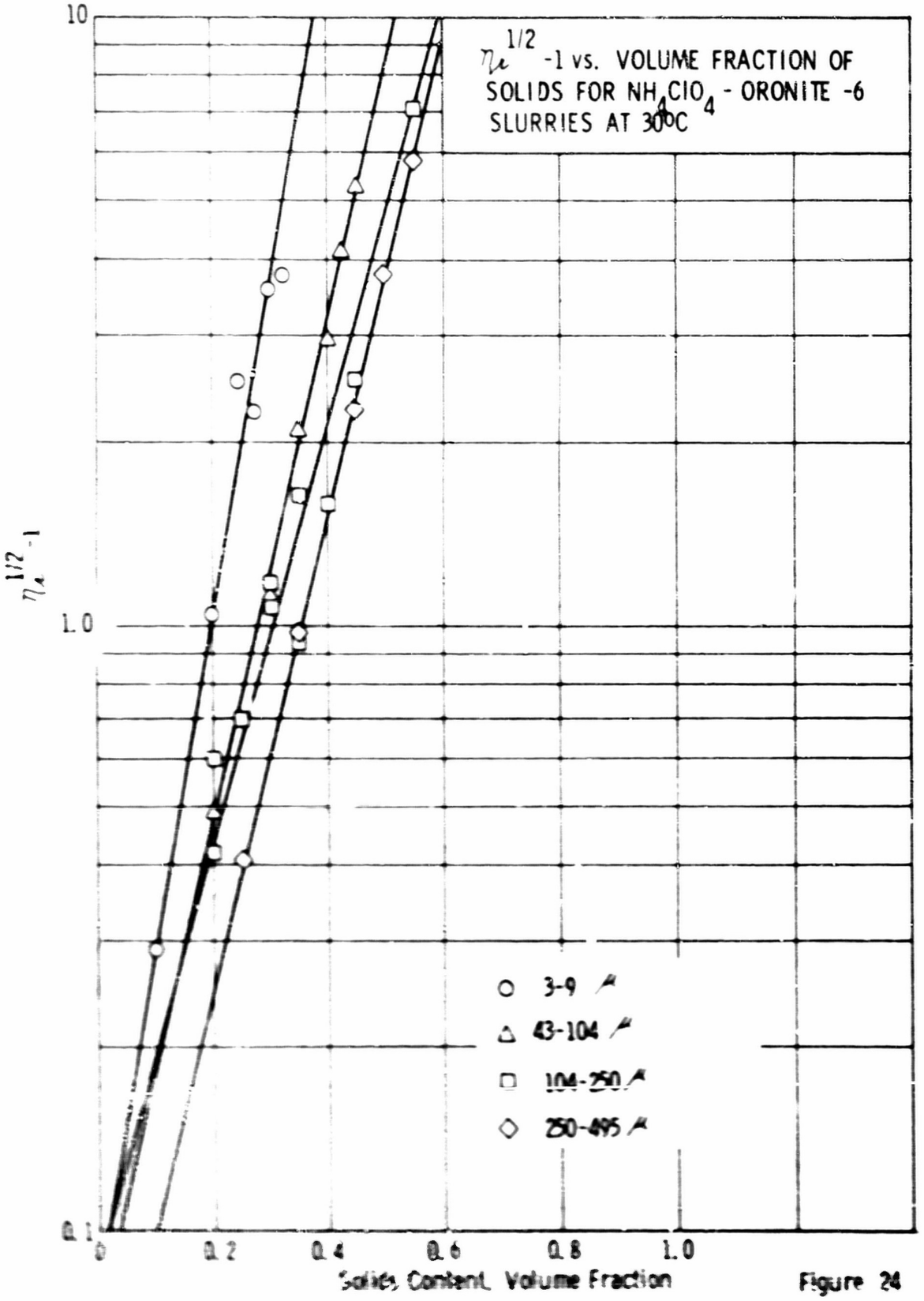

$\eta_e^{1/2}$ -1 vs. VOLUME FRACTION OF SOLIDS FOR NH_4ClO_4 - ORONITE -6 SLURRIES AT 30°C
$\eta_s^{1/2}$ -1
10
1.0
0.1
0
0.2
0.4
0.6
0.8
1.0
Solids Content, Volume Fraction
○ 3-9 μ
△ 43-104 μ
□ 104-250 μ
◇ 250-495 μ

Figure 24

Table 23

(U) VARIATION OF CONSTANTS C AND D WITH PARTICLE SIZE

Particle Size,	Solids Content Vol. Fraction	C	D
3-9	0.10 - 0.325	5.57	-0.11
43-104	0.20 - 0.45	4.18	-0.154
104-250	0.20 - 0.55	3.40	-0.03
250-495	0.25 - 0.55	3.89	-0.112

The physical significance of the parameters C and D are not apparent.

C. (U) PHASE II

1. (U) Introduction

Phase II will involve preliminary study of the compatibility of the candidate prepolymer, curing agents, or suitable models with advanced oxidizers and fuels. Materials which are compatible will be tested in propellants.

2. (U) Use of Model Systems

The use of model compounds to study the chemical interaction between binder components and oxidizers or fuels has proven to be a powerful tool. The model compound allows the chemist to carry out analyses which are difficult or impossible to achieve with the prepolymers and curing agents used to prepare propellants. The result is that not only are incompatibilities uncovered, but information concerning the nature of the incompatibility is obtained.

The model compound or compounds should be a low molecular weight replica of some structural or chemical characteristic of the prepolymer or curing agent. It is not always necessary that a single model show all the characteristics of its counterpart. In some cases it is expedient and convenient to use several models each showing only one characteristic of the material of interest. This approach has been used in this program where 3 model compounds are used to describe the chemical behavior of Telagen S.

A useful characteristic of the model compound is its volatility so that analysis by gas-liquid chromatography is possible. GLC is a powerful method for discovering and studying unexpected chemical interactions. All the models used in this program have this property.

3. (U) Model Compounds

Three compounds were used as models for the hydroxy terminated Telagen S. These were 2-octanol (J.T. Baker Chemical Co., 99% pure by GLC), 1-decanol (Eastman Kodak Co., white label, pure by GLC) and 1,7-octadiene (Columbian Carbon Company, used as received). The first two compounds represent the primary and secondary hydroxy groups of the prepolymer while the olefin is characteristic of the residual unsaturation. In a similar fashion the carboxy terminated Telagen S was represented by 1-nonanoic acid (Emery Industries Inc., redistilled, b.p. 129°C/5 mm; pure by GLC), 2-ethylhexanoic acid (Union Carbide Corp., pure by GLC and used as received) and 1,7 octadiene.

Phenyl isocyanate (Eastman Kodak Co., white label; redistilled b.p. 166°C; pure by GLC) was used as a model isocyanate and the solvents, n-hexane (Fisher Scientific Co., spectroanalyzed grade) and toluene (J. T. Baker, reagent grade; distilled from sodium) were used to represent the hydrocarbon portions of

of Telagen S. Bibenzyl, toluene and phenylcyclohexane were used as internal markers for the GLC studies.

4. (U) Method for Studying Compatibility of Fuels with Model Compounds

The samples were prepared in a tared 1 dram shell vial within a weighing bottle. The tared bottle and vial were put into a dry nitrogen atmospheric box where the fuel sample was put into the shell vial. The weighing bottle was sealed, removed from the atmospheric box in order to weigh the fuel and then returned to the dry box. The shell vial was fitted with a rubber serum cap after introduction of 0.5 ml of a solution containing a model compound, and removed from the box for gas chromatographic analysis. Figures 25 through 28 show chromatograms for the model compounds.

Stored or heated, samples were sealed into 2 ml ampules prepared essentially by the method described above.

The gas chromatographic analysis of the model compounds were performed on an F & M Model 500 Gas Chromatograph equipped with a katharometer detector. A sample size of 10 μl was used for each analysis. Table 24 shows the column conditions used for the separations.

5. (U) Compatibility of Model Hydroxy Compounds with Advanced Fuels

Solutions of the various model compounds were added to the solid fuels and periodically analyzed by gas chromatography for concentration changes.

The alcohols, 2-octanol and 1-decanol were compatible with LMH-1, and chrome passivated Be at 50°C for 18 hours (Table 25).

GAS-LIQUID CHROMATOGRAM OF A TOLUENE SOLUTION OF BIBENZYL, 2-OCTANOL, AND 1-DECANOL

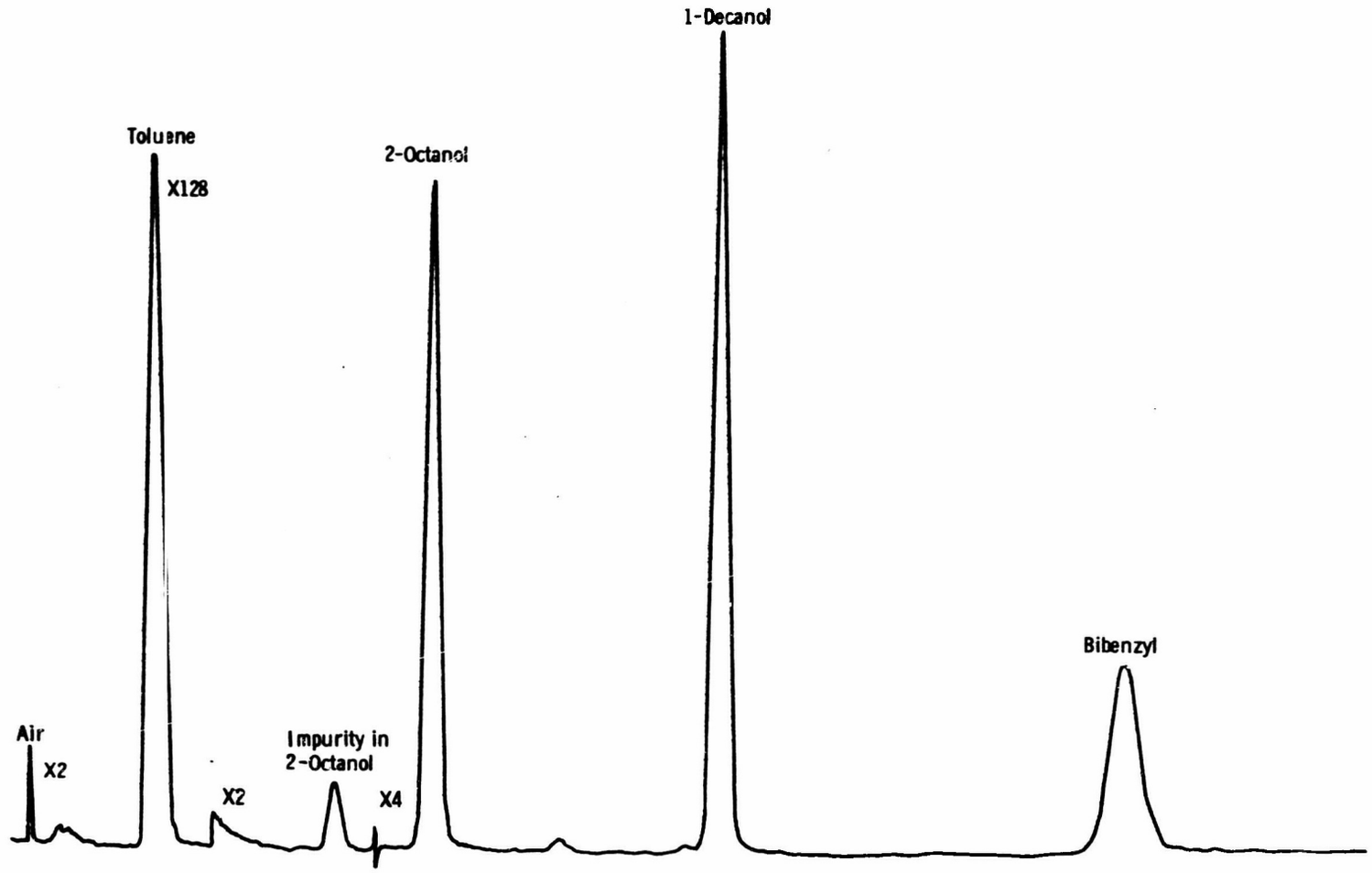


Figure 25

GAS-LIQUID CHROMATOGRAM OF A HEXANE SOLUTION OF TOLUENE AND 1,7-OCTADIENE

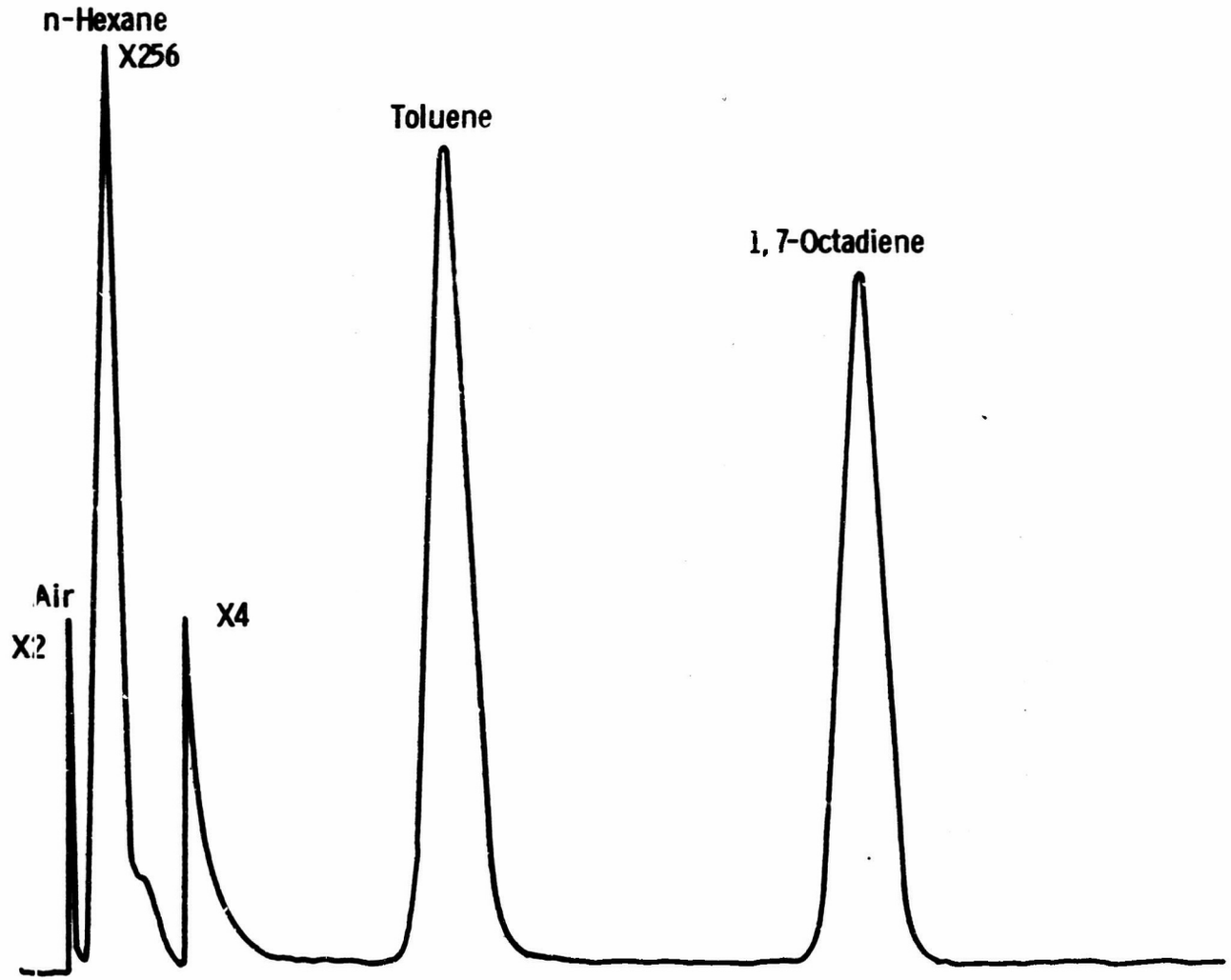


Figure 26

GAS-LIQUID CHROMATOGRAM OF A TOLUENE SOLUTION OF PHENYLCYCOHEXANE, 2-ETHYHEXANOIC ACID AND NONANOIC ACID KEPT OVER CHROME PASSIVATED Be FOR 18 HOURS AT AMBIENT TEMPERATURE

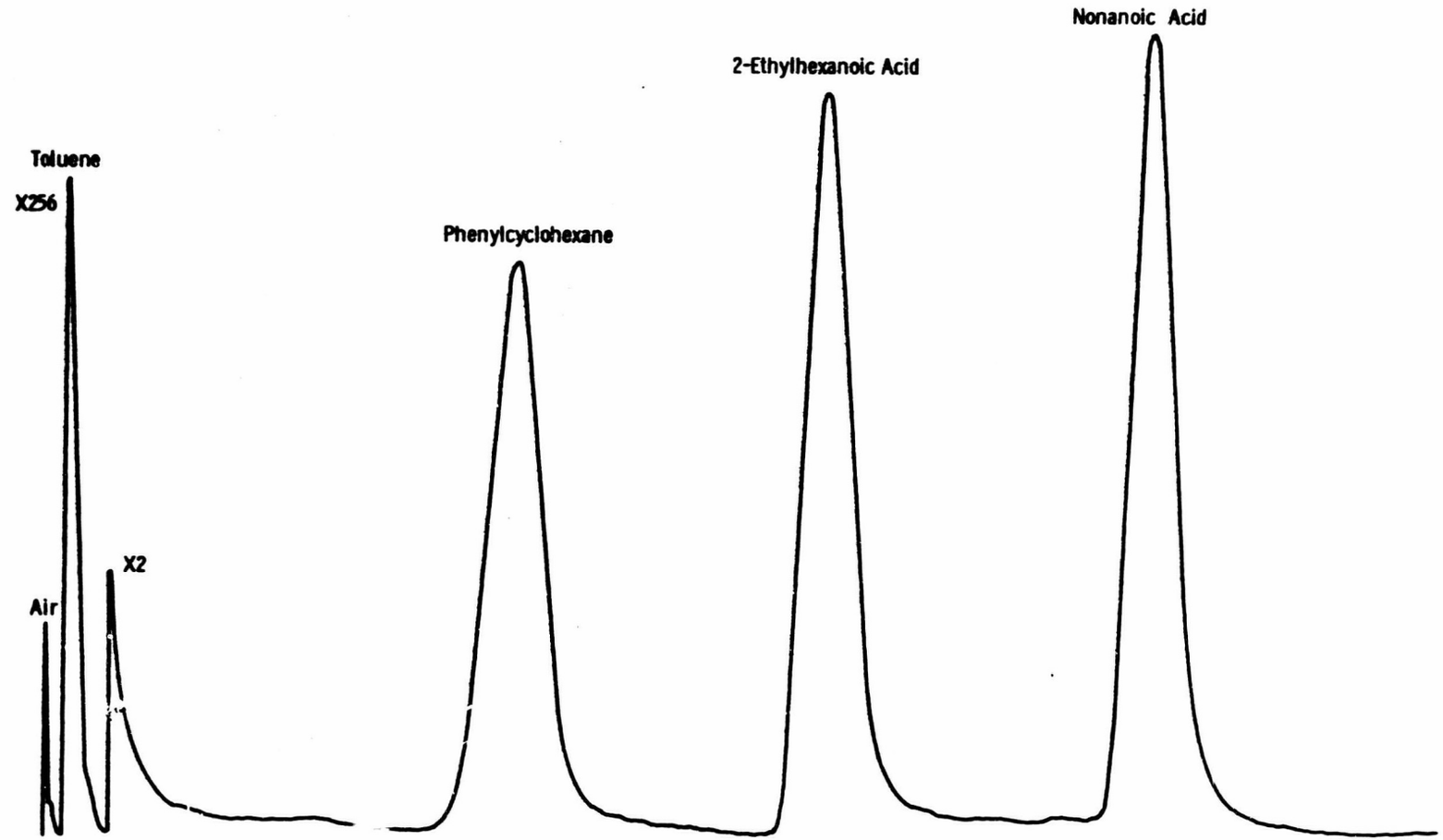


Figure 27

GAS-LIQUID CHROMATOGRAM OF A TOLUENE SOLUTION OF PHENYL ISOCYANATE AND PHENYLCYCLOHEXANE

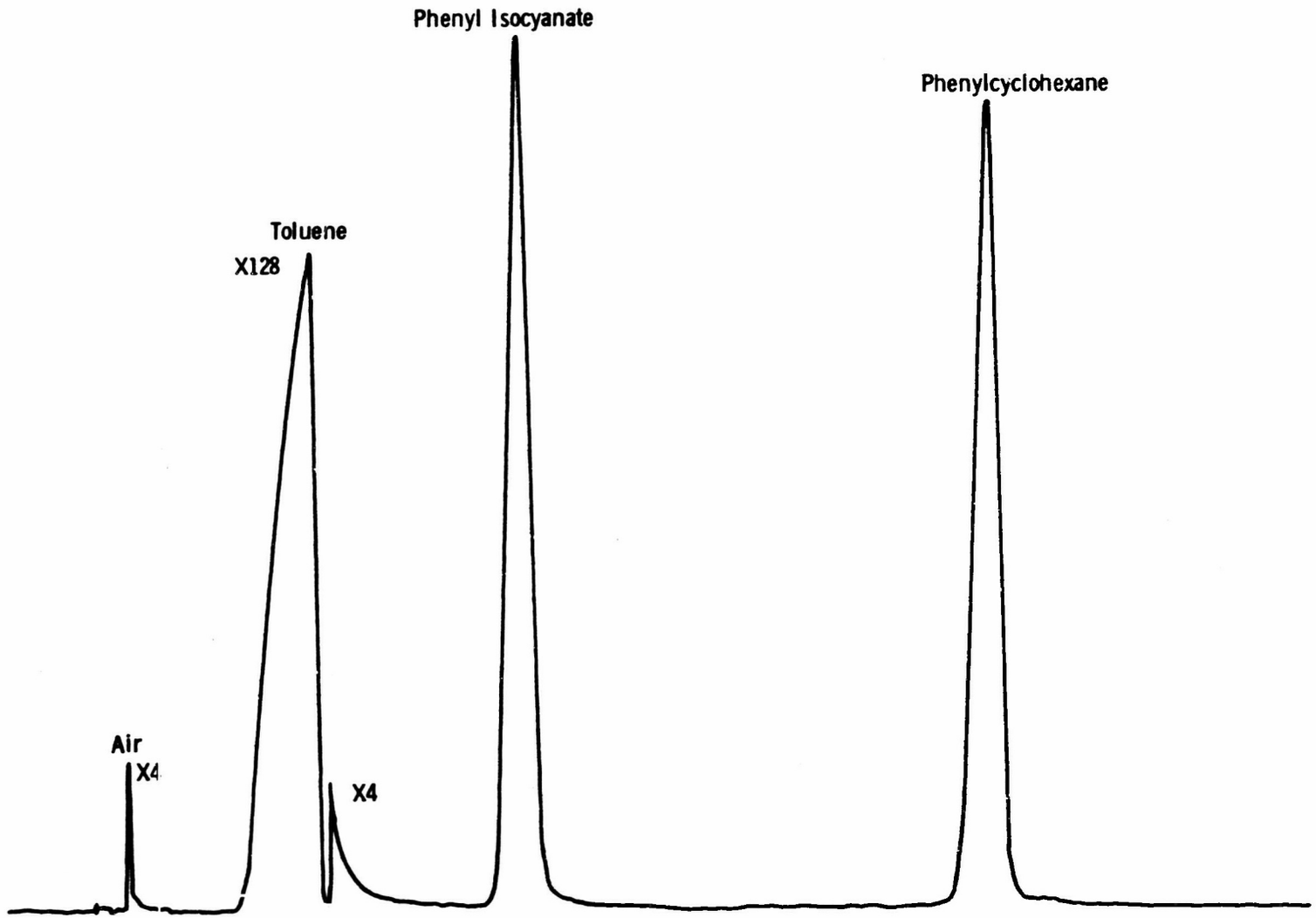


Figure 28

Table 24

(U) CHROMATOGRAPHIC CONDITIONS FOR ANALYSIS OF MODEL SYSTEMS BY GLC

	Material Analyzed			
	Alcohols	Olefins	Acids	Isocyanates
Column Material	1[a]	1[a]	2[b]	3[c]
Temperature, °C	100-200	50-75	100-150	55-134
Heating Rate, °C/min	15	21	7.9	15
Gas Flow, ml/min	100	100	20	60
Injection Port Temp., °C	200	190	200	200
Block Temp., °C	300	300	300	300
Bridge Current, ma	150	150	150	150

[a] 4' x 1/4" stainless steel; 10% Carbowax on 60-80 mesh Diatoport S.

[b] 2' x 1/4" stainless steel; 10% ethylene glycol succinate on 60-80 mesh Diatoport S.

[c] 2' x 1/4" stainless steel; 10% silicone gum rubber SE-30 on 60-80 mesh Diatoport S.

Table 25

(U) COMPATIBILITY OF 2-OCTANOL AND 1-DECANOL WITH ADVANCED FUELS[a]

		LMH-1			Be		
Time, hr	Temp, °C	LMH-1: Alcohol	$C_8H_{17}OH$	$C_{10}H_{21}OH$	Be: Alcohol	$C_8H_{17}OH$	$C_{10}H_{21}OH$
0	-	4.6	800	616	3.5	795	616
18	23	4.6	800	610	3.5	795	616
18	50	6.5	800	615	5.1	786	615
18	50	2.7	800[b]	622[b]	-	-	-

[a] Values are areas under the GLC elution peaks relative to a value of 400 for bibenzyl used an internal standard; accuracy ± 1%.

[b] Freshly ground LMH-1.

6. (U) Compatibility of Model Olefin with Advanced Fuels

The unsaturated compound, 1,7-octadiene, showed a slight decrease in concentration, about 3%, after 18 hours at 50°C in the presence of the same fuels (Table 26). No new compounds were detected by gas chromatography and no gas evolution was observed.

Table 26

(U) COMPATIBILITY OF 1,7-OCTADIENE WITH ADVANCED FUELS[a]

		LMH-1		Be	
Time, hr	Temp °C	LMH-1: Olefin	GLC Area	Be: Olefin	GLC Area
0	-	8.8	949	18.5	925
18	23	8.8	938	18.5	925
18	50	8.7	907	18.9	909

[a]Values are areas under the GLC elution peaks relative to a value of 1000 for toluene used as an internal standard; accuracy ± 2%.

7. (U) Compatibility of Model Carboxy Compounds with Advanced Fuels

The carboxylic acids, nonanoic acid and 2-ethylhexanoic acid indicated some reactivity with LMH-1, but not with the passivated Be (Table 27). The branched carboxylic acid, 2-ethylhexanoic acid, was stable even after 18 hr at 50°C on freshly ground LMH-1, whereas the nonanoic acid showed a 3% decrease in concentration on the unground LMH-1 and a 10% change on the freshly ground LMH-1 under the same reaction conditions. Gaseous evolution was observed, especially with the ground LMH-1, but no new products were detected by gas chromatography. It is concluded from these observations that neutralization of the acid was occurring.

Table 27

(U) COMPATIBILITY OF NONANOIC AND 2-ETHYLHEXANOIC ACIDS WITH ADVANCED FUELS[a]

		LMH-1			Be		
Time, hr	Temp, °C	LMH-1: Acid	$C_8H_{17}COOH$	$C_7H_{15}COOH$	Be: Acid	$C_8H_{17}COOH$	$C_7H_{15}COOH$
0	-	3.5	2280	2230	4.4	2210	2135
18	23	3.5	2275	2240	4.4.	2190	2140
18	50	4.4	2208	2228	5.4	2212	2215
18	50	3.8[b]	2060[b]	2195[b]	-	-	-

[a]Values are area under the GLC elution peaks relative to a value of 2000 for phenylcyclohexane used as an internal standard; accuracy ± 1%.

[b]Freshly ground LMH-1.

8. (U) Compatibility of Model Isocyanate with Advanced Fuels

The hydroxy terminated Telagen S is cured with isocyanates. The compatibility of pheryl isocyanate, the model compound for the curing agents, with the advanced fuels is summarized in Table 28. The isocyanate was reactive in the presence of the fuels showing a decrease of 8.6% on LMH-1 and 26.4% on chrome coated Be after 18 hours at 50°C. Gas evolution was noted in the case of LMH-1, but no new products were observed for either case by the gas chromatography.

Table 28

(U) COMPATIBILITY OF PHENYL ISOCYANATE WITH ADVANCED FUELS[a]

		LMH-1		Be	
Time, hr	Temp, °C	LMH-1: C_6H_5NCO	GLC Area	Be: C_6H_5NCO	GLC Area
0	-	11.0	907	12.5	908
48	23	9.3	823	10.0	726
18	50	12.0	829	15.0	669

[a]Values are areas under the GLC elution peaks relative to a value of 1000 for phenylcyclohexane used as an internal standard; accuracy ± 1%.

9. (U) Compatibility of Telagen S and the Workhorse Binder with Advanced Fuels

Hydroxy terminated Telagen S showed no adverse effects in the presence of chrome coated Be, LMH-1 or LMH-2, i.e., no gassing or viscosity increase.

Binders were prepared using CTI, hexamethylene diisocyanate and hydroxy terminated Telagen S (0.32:0.71:1.0 eq) with an equal weight of Be and LMH-1. In the case of LMH-2 a 2:1 weight ratio of binder to LMH-2 was used because of mixing difficulties. After six days at 50°C, the binders with Be and LMH-2 were hardening but the sample with LMH-1 was gassing. These results are consistent with the model studies and point to incompatibility of the NCO group with LMH-1.

Tests with a number of plasticizers indicated good compatibility with TMETN ($CH_3C(CH_2ONO_2)_3$), NEMNC ($O_2NOCH_2CH_2OCON(NO_2)CH_3$) and IDP and incompatibility with BDNPA-BDNPF (1:1) and ADN ($NC(CH_2)_4CN$).

Binders with IDP and the advanced fuels were prepared. After six days at 50°C, the binder with LMH-1 was gassing. The others were curing normally; the binder with LMH-2 being twice as hard as the binder with Be.

10. (C) Theoretical Specific Impulse for Hydroxylammonium Perchlorate

In preparation for future compatibility studies with HAP, thermodynamic calculations were made for the systems involving this oxidizer with aluminum and the workhorse binder. The results in Figures 29-32 include similar calculations for the analogous unsaturated binder.

The unsaturated analogue shows an expected advantage in theoretical impulse because of the higher heat of formation of the unsaturated binder (-7.848 kcal/100g compared to -46.9615 kcal/100g for the saturated binder).

For systems utilizing the workhorse binder, the HAP to binder ratio of interest would be about 7:1.

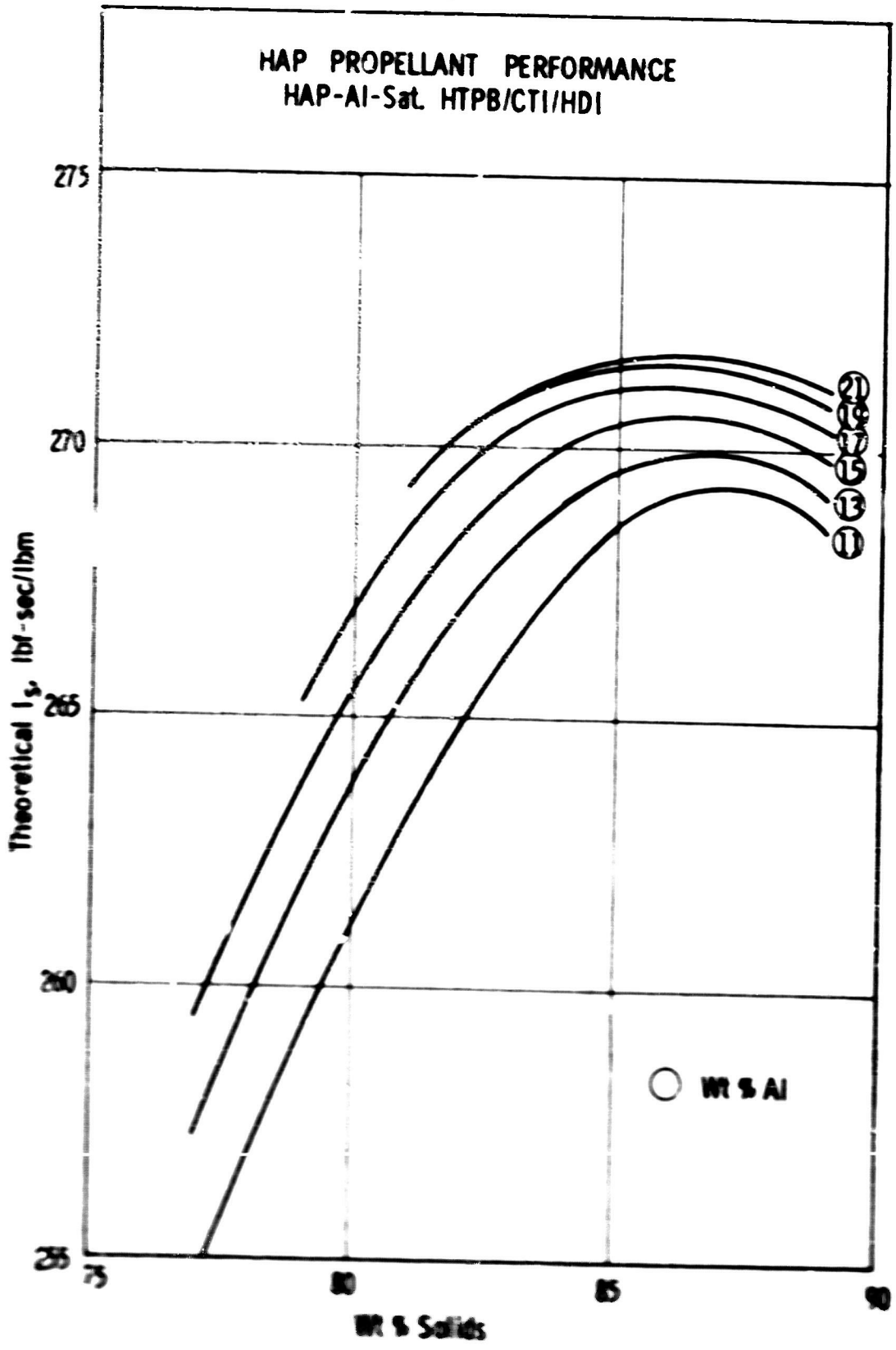

HAP PROPELLANT PERFORMANCE
HAP-Al-Sat. HTPB/CTI/HDI
275
270
265
260
255
Theoretical I_{sp}, lbf-sec/lbm
21
19
17
15
13
11
Wt % Al
75
80
85
90
Wt % Solids

Figure 29

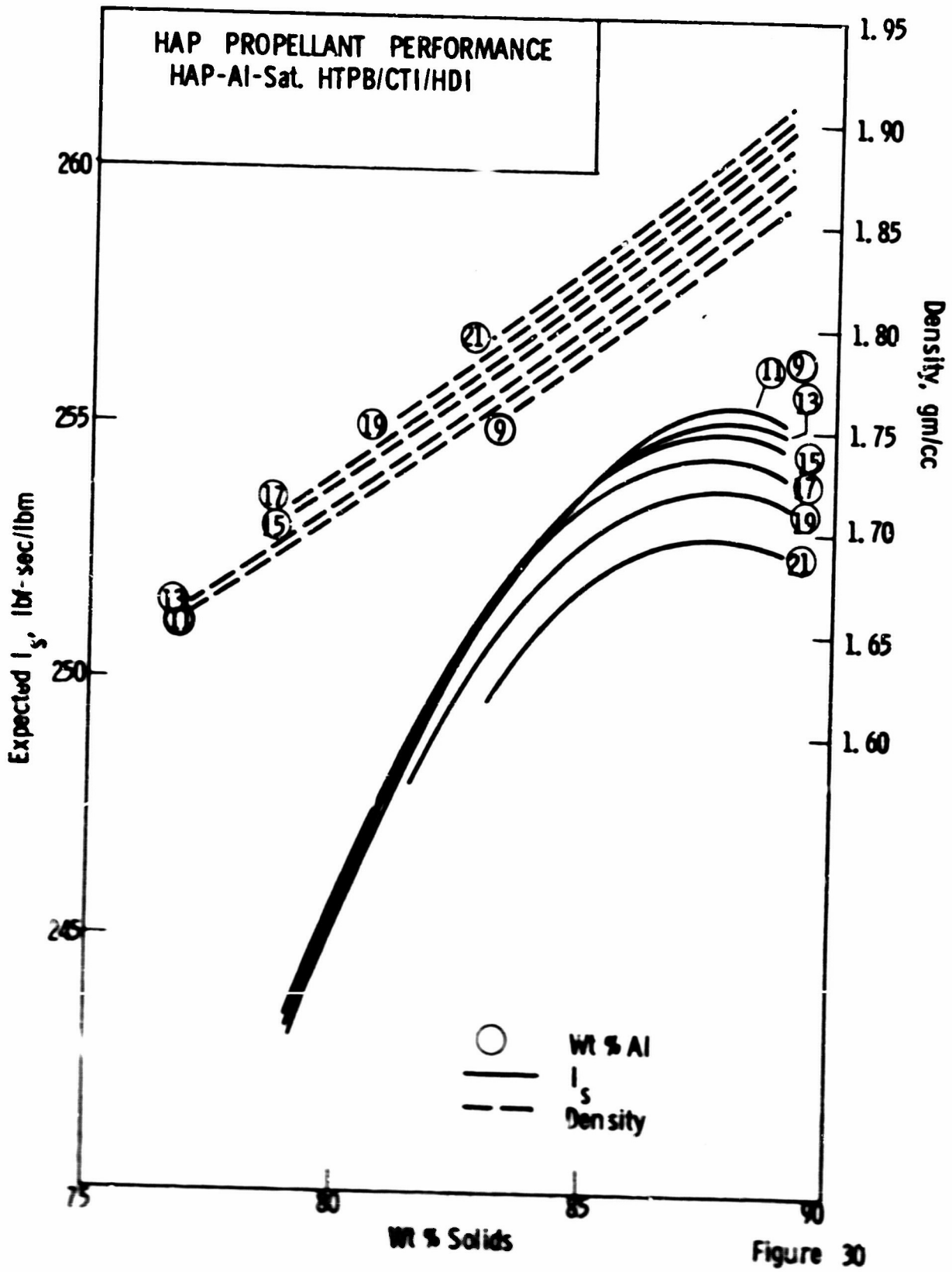

HAP PROPELLANT PERFORMANCE
HAP-Al-Sat. HTPB/CTI/HDI
260
255
250
245
Expected I_s, lbf-sec/lbm
1.95
1.90
1.85
1.80
1.75
1.70
1.65
1.60
Density, gm/cc
75
80
85
90
Wt % Solids
Wt % Al
I_s
Density

Figure 30

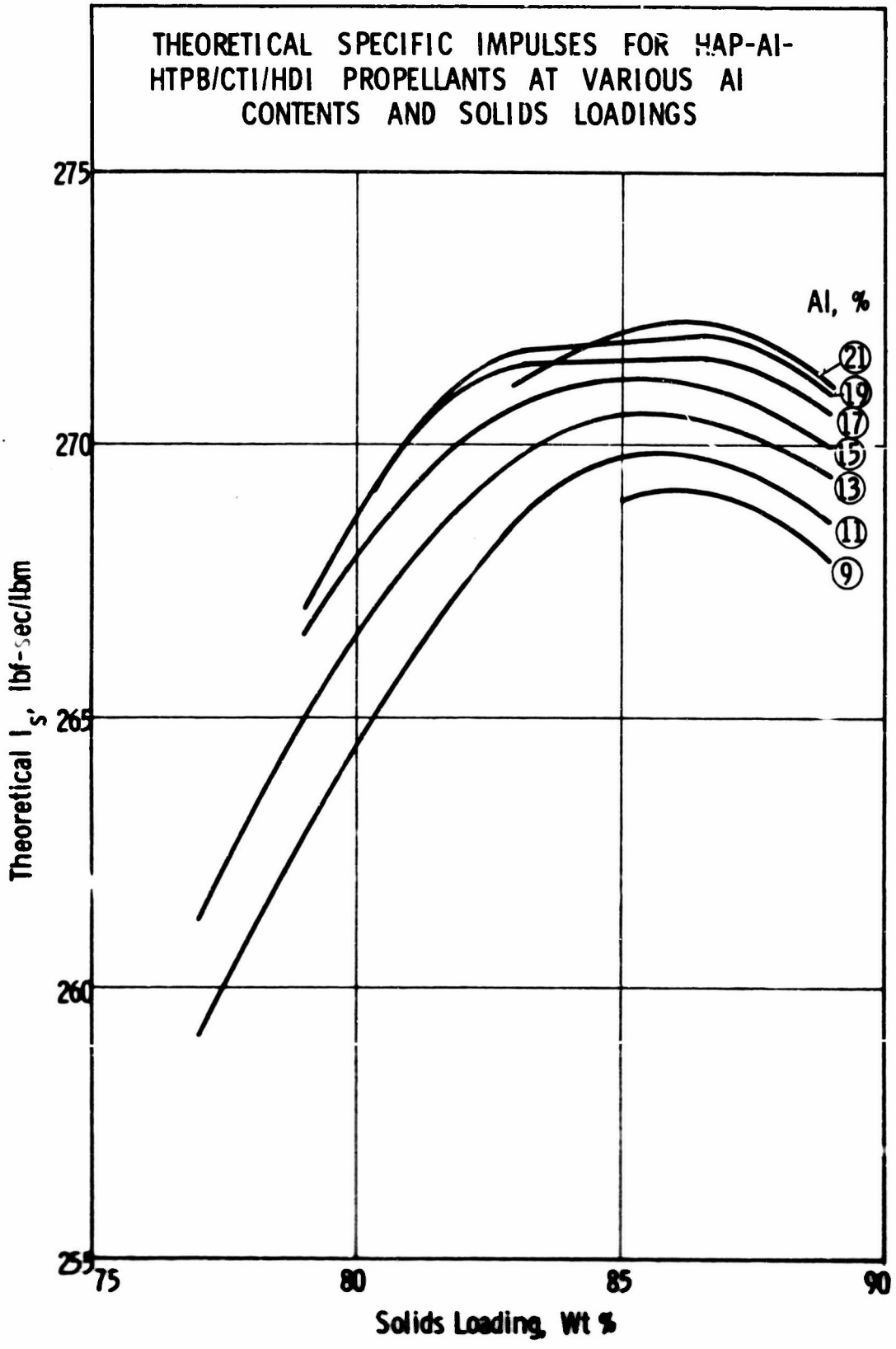

THEORETICAL SPECIFIC IMPULSES FOR HAP-AI-HTPB/CTI/HDI PROPELLANTS AT VARIOUS AI CONTENTS AND SOLIDS LOADINGS
Al, %
21
19
17
15
13
11
9
Theoretical $I_{s'}$, lbf-sec/lbm
275
270
265
260
255
75
80
85
90
Solids Loading, Wt %

Figure 31

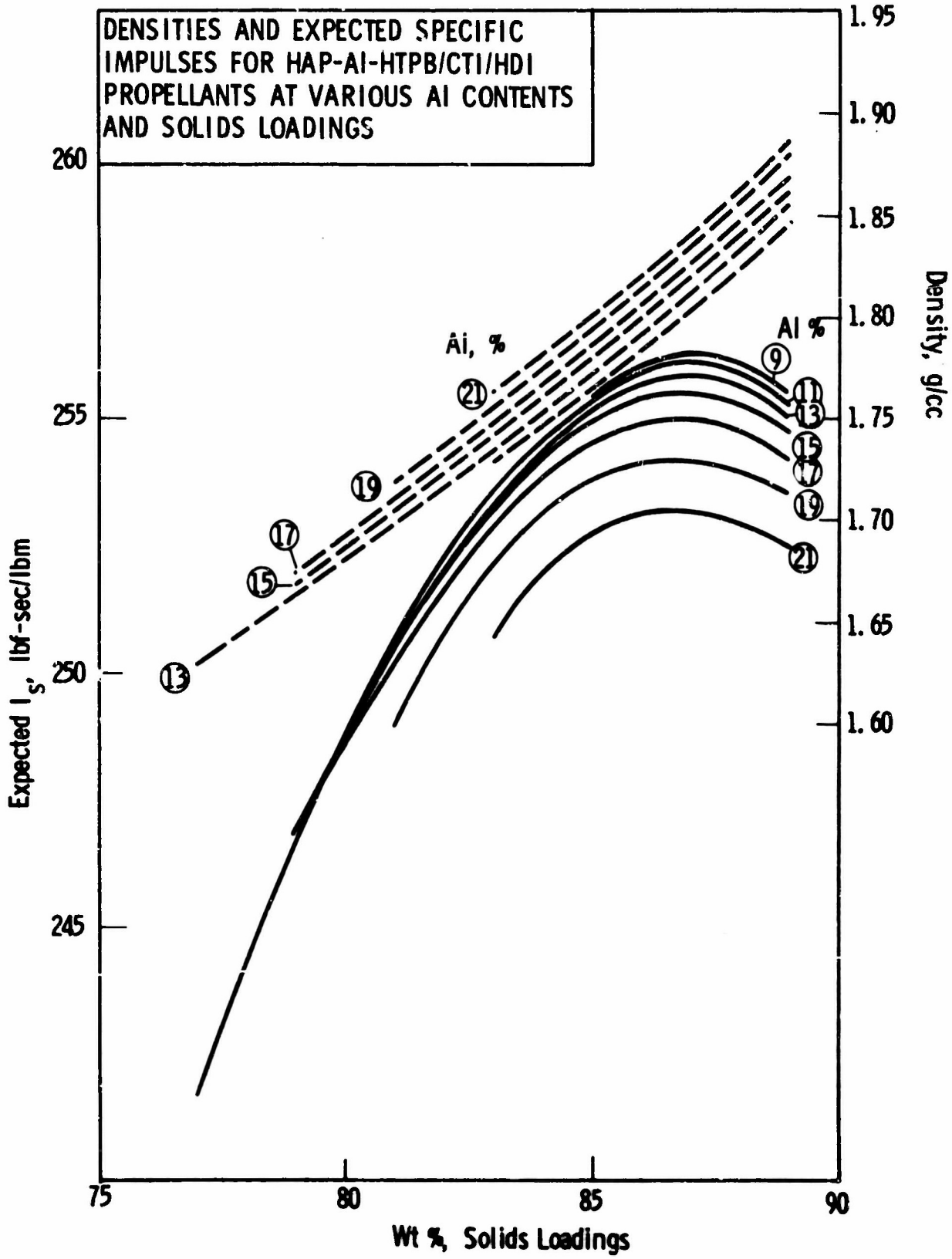

DENSITIES AND EXPECTED SPECIFIC IMPULSES FOR HAP-Al-HTPB/CTI/HDI PROPELLANTS AT VARIOUS Al CONTENTS AND SOLIDS LOADINGS
Ai, %
Al %
Expected $I_{s'}$, lbf-sec/lbm
Density, g/cc
Wt %, Solids Loadings
260
255
250
245
1.95
1.90
1.85
1.80
1.75
1.70
1.65
1.60
75
80
85
90
9
11
13
15
17
19
21

Figure 32

CONFIDENTIAL

Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)	2a. REPORT SECURITY CLASSIFICATION
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b. PROJECT NO. 3418	
c.	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) 1030-81Q-1
d.	

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11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	Air Force Rocket Propulsion Laboratory Research and Technology Division Edwards, California Air Force Systems Command, United States Air Force

13. ABSTRACT

(U) The investigation and characterization of the saturated hydrocarbon binder developed under Contract AF 04(611)-10386 for use in solid rocket propellant were continued. The molecular weight and functionality distributions were determined for the saturated hydrocarbon prepolymer. The functionality of the prepolymer was independent of the molecular weight. Recrystallization was better than distillation for purifying the isocyanate crosslinking agent. While NH_4ClO_4 was compatible with the isocyanate curing agents, many plasticizers were not. Of the plasticizers, the hydrocarbon oils were most compatible. Treatment of the plasticizers with molecular sieves or by passing through a column of silica gel improved the compatibility. The incompatibility of the curing agents and the plasticizers affected both the mechanical behavior of binders and propellants and the gel fraction of toluene swollen binders. The low temperature properties of the binders were not adequate for solid propellants useful at low temperatures although the glass transition temperatures of the binders were lower than -100°F. Carbon tetrachloride and tetrahydrofuran gave the maximum swelling ratios with the "workhorse" binder.

(C) The compatibility of the prepolymer and model compounds with beryllium, beryllium hydride and aluminum hydride was determined. The most difficulty involved aluminum hydride and phenyl isocyanate, a model compound, for the curing agent. Binders containing aluminum hydride gassed. Thermodynamic calculations of the expected performance of hydroxylammonium perchlorate, aluminum, "workhorse" binder systems were made.

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Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Saturated Hydroxy Terminated Polybutadienes						
Saturated Carboxy Terminated Polybutadienes						
Effect of plasticizers on Isocyanate Curing Agents						
Effect of Pretreated Plasticizers on Isocyanate Curing Agents						
Effect of Plasticizer-Isocyanate Interaction on Mechanical Behavior of Urethane Binders						
Effect of Plasticizer-Isocyanate Interaction on Gel Fraction of Urethane Binders						
Effect of Plasticizer-Isocyanate Interaction on Mechanical Behavior of Urethane Propellants						
Effect of Fillers on Viscosity of Liquids.						
Viscosity of NH_4ClO_4-Oronite-6 Slurries						
Compatibility of Advanced Fuels with Saturated Polybutadienes						

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